A Study of Metal Speciation Using a Two-Stage Electrothermal Atomizer. Laser Infrared Fluorescence as a Gc Detector.

Peter L. h Jowett
Louisiana State University and Agricultural & Mechanical College

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A STUDY OF METAL SPECIATION USING A TWO-STAGE ELECTROTHERMAL ATOMIZER. LASER IR FLUORESCENCE AS A GC DETECTOR

The Louisiana State University and Agricultural and Mechanical Col. Ph.D. 1982

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A STUDY OF METAL SPECIATION USING A
TWO-STAGE ELECTROTHERMAL ATOMIZER.
LASER IR FLUORESCENCE AS A GC DETECTOR.

A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
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in partial fulfillment of the
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Doctor of Philosophy

in

The Department of Chemistry

by

Peter L. H. Jowett
B.Sc., Fort Lewis College, 1973
M.Sc., Louisiana State University, 1977
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ABSTRACT

A. A study of metal speciation using a two-stage electrothermal atomizer.

A two-stage atomic absorption atomizer has been designed and built. It consisted of a molybdenum tube atomizer maintained at high temperatures (2200°C for example) and a molybdenum tube vaporizer which was gradually heated from room temperature up to high temperatures. A sample was placed within the latter section when it was cool, and while the former was heated. Subsequently, the vaporization section was gradually heated and the evolved gases were entrained by the carrier gas through the atomization section and into the optical lightpath. Atomic absorption versus temperature curves were obtained for Pb, Zn and Cd compounds. The resultant data were similar in many respects to those obtained by conventional thermal analysis but at much lower concentrations (or about $10^{-8}$ g).

Low temperature peaks were observed using the two-stage atomizer indicating atomization of salts volatilized at low temperatures. A similar study with a PE*403 graphite furnace revealed no low temperature peaks, presumably because atomization at low temperatures was not achieved.

Solutions of lead halides gave peaks corresponding to the vaporized lead halide as well as to the oxide. Similar results were also observed with cadmium solutions. These gave an indication of the form of the metal compounds that was being volatilized from each solution.

Lead in air particulates appeared to be present as the oxide
and other unidentified forms. This preliminary study indicated that the technique shows high potential for speciation of metal salts at low concentrations.

B. Laser induced IR fluorescence as a GC detector.

Following encouraging work on remote sensing of atmospheric pollutants using laser induced IR fluorescence, the phenomenon was studied as an in situ GC detector. Results showed that collision deactivation on the walls of the detector greatly reduced fluorescence intensity. This essentially vitiated the uses of this technique as a sensitive, continuous flow GC detector.
PART I

AN ELECTROTHERMAL TWO STAGE ATOMIC ABSORPTION ATOMIZER FOR SPECIATING INORGANIC SALTS

1.-INTRODUCTION.

For many years man has sought to understand his environment whether simply out of curiosity or because of desire. The latter has often been driven by man's continuous quest to improve his health and material welfare. In the process, many abuses of nature have occurred often out of ignorance or lack of concern. Only in the last few decades have any serious efforts been undertaken to curb or control these detrimental activities.

Many such activities are being regulated especially when they intrude in the lives of others, but these regulations are sound when insight is available. One important area concerns pollutants released into the environment from existing and emerging industries, or natural sources. For example, it is important to understand how a volcano eruption or the persistence in the atmosphere of compounds emitted from automobiles might affect the environment. Much effort has already been channeled into the identification of such released materials, and results have been compiled providing a better picture of our environment.

A specific example of the studies necessary for proper regulations is provided with the air that we breathe. We know that we must keep it clean, but we must also look at the repercussions on the whole system that the emission of gases or particulates might have. In doing so a
systematic observation of many parameters has been undertaken. For example, it is important to know the source of particulate emissions; observing their reactivities in the atmosphere will also provide information as to the potential harm or benefit that these have on man and the environment. Collecting particulate samples for analyses is often achieved by any number of methods and often involve separating them by size or chemical form.

The same comments apply to water pollution resulting from short term injection (dumping or precipitation), or by slow exposure over the years (as leaching from the ground).

A. Speciation.

Speciation is the determination of the physico-chemical forms of an element or compound. It is often insufficient to measure the total amount of an element present in a sample. It is frequently necessary to go a step further and specifically identify the chemical form of the metal. Much work has already been done in the speciation of organic material, such as distinguishing between similar compounds such as styrene and styrene oxide (thought to be a suspected carcinogen). Another example of speciation is the distinction between geometric isomers like fumaric acid and maleic acid (the latter being toxic\(^1\)); or benzo(a)-pyrene which is carcinogenic, benzo(e)-pyrene which is thought to be a mutagen and a promoter/cocarcinogen\(^2\), and pyrene a suspected mutagen. There also are many cases involving biologically important compounds where only one of the isomers might be biologically active, while the others are not.
B. Techniques for speciation of organic compounds.

Some of the more recently used techniques in which organic compounds were being speciated, include the use of gas chromatography with flame ionization as detector (GC-FID) to monitor hydrocarbons in the ambient air (including total and non methane hydrocarbons); Fourier transform infrared has been coupled to gc, and capillary gc, and have become powerful tools for compound speciation. An excellent review article concerning GC-FTIR is available by Erickson in which he also discusses, double beam GC-FTIR. Another example of a non-metal speciation technique is the coupling of liquid chromatography with FTIR (LC-FTIR), both in the gel permeation (GPC) and normal adsorption modes, to look at parafin oil components. Others have used mass spectrometry as a LC detector (LC-MS), and the use of an LC-micro MS has also been reported. The interfacing of these techniques has been quite challenging, but they have been used to monitor some airborne polycyclic aromatic hydrocarbons (PAH).

Another method is LC-$^1$HNMR used to identify hydrocarbons in petroleum and synthetic fuels, in an on-line mode, or continuous flow. (Other NMR nuclei have also been tried).

Laser fluorimetry as an LC detector has also been used with microcolumns. Some examples of this approach include measuring low levels of porphyrins and low levels of zearalenone in corn (potent estrogenic microtoxin, suspected of causing infertility in cattle and swine). Similarly, thin layer chromatography was used to measure very low levels (pg amounts) of aflatoxins. Review publications of this approach have been published which discuss the applications to the
analyses of several organic compounds such as drugs, antitumor agents, coal constituents and the like.

Another interesting chromatography detector has been the use of piezoelectric crystals in GC.\textsuperscript{18} They have been used to monitor organic gases in ambient air\textsuperscript{19}. Their use in LC is also being investigated and is in the early stages of development.\textsuperscript{20}

One interesting technique, in speciation, is that of FT-MS which has been coupled to capillary GC.\textsuperscript{21,22} The use of MS units in tandem is also a powerful approach and is being used to a considerable extent now.\textsuperscript{22} Wilkins et al.\textsuperscript{23} have combined GC-FTIR-MS to analyze organic samples.

C. Methods for metal speciation.

Some examples illustrating the need for metal speciation include the oxidation state dependency of antimony and chromium in their toxicological effects. Numerous studies attempting to correlate the toxicity of one form over another have been reported. Other studies have linked arsenic trioxide to lung cancer whereas organoarsenicals have not been linked to carcinogenicity. There also have been considerable studies correlating the presence of chelating agents in the waterways with the toxicity and concentration of metal free ions in them. Some examples of these bioassay studies include correlating the toxicity of zinc ions to algae, rather than the total amount of water soluble metal (including the complexed form)\textsuperscript{24}. In the same way, free cadmium ions were correlated to the intoxication of grass shrimp.\textsuperscript{25} In a few cases it has been found that some complexing agents actually
increase the uptake of a metal.\textsuperscript{26,27} Therefore, it becomes quite evident that knowing the total metal concentration in a particular sample, such as water or air, can only partially tell us about a toxicity problem that might exist. Speciation of the metal chemical forms is essential. Thus it could be possible to tolerate a high metal concentration as long as the toxic form was at low levels.

Our attention will be focused on the speciation of metal compounds, both organometallic or inorganic in nature. To accomplish this at low levels is a challenge to analytical instrumentation. Although metal speciation analysis is a relatively recent field, many different approaches have been taken and these many innovations will be described in three broad categories: chemical separation schemes, which may be coupled to instrumental methods; instrumental techniques, mostly emphasizing the coupling of these and; speciation as a result of thermal degradation of samples.

\textbf{Cl. Chemical Separation.}

Examples of the separation of metals using extraction, precipitation and hydride generation will be given in this section. One important application in the use of chemical separation for metal speciation has been the development of methods for speciating arsenic. This has been brought about because of the different toxicity effects that arsenites and arsenates each have, and which are themselves different from those of organoarsenicals. (Arsenic is mostly used in agriculture as herbicides, pesticides, and wood and cotton preservatives.)

Adams et al.\textsuperscript{28} developed a procedure in which they used ammonium
sec-butyldithiophosphate in hexane as solvent, to selectively preconcentrate arsenic (III) from water samples and then back-extracting it into water, with subsequent analysis by atomic absorption spectrometry (AAS). Arsenic (V) was chemically reduced and then analyzed separately following the same procedure. Another example of a more specific method for arsenic speciation is that reported by Braman et al. 29 in which nanogram levels of arsines were detected in water samples. Their procedure consisted of reducing arsenic compounds in pH buffered solutions as the arsenite and arsenate ions, methylarsonic and dimethylarsinic acids. Reduction was accomplished with the addition of sodium borohydride. Arsenic (III) was reduced at pH 3.5-4, and the other forms at pH of 1-2. The respective arsines were trapped at liquid nitrogen temperatures and subsequently were individually released as the collection tube was heated over a 1-2 minute period. Final detection was done by atomic emission from a d.c. electric discharge. The authors also reported using the method to analyze biological samples 30, as well as filtered air and particulate samples 31.

A similar approach to the speciation of arsenic was reported by Howard and Arbab-Zavar 32 where the inorganic and organic species were trapped as arsines, and then selectively volatilized into the optical path of an atomic absorption system. They also reported the interferences suffered by the presence of several metals.

Another example of chemical separation as a means of metal speciation is that proposed by Han-Wen, Xiao-Quan and Zhe-Ming 33. In their procedure they were able to differentiate antimony (III) from the (V) state by first extracting the former in chloroform-BPHA (N-benzoyl-N-phenylhydroxylamine), over wide pH range without interference of
antimony (V). The extract then was analyzed by AAS using copper as a matrix modifier. It increases the appearance temperature of antimony, therefore allowing a higher ashing temperature of about $1000^\circ$ or above; this effect is believed to be due to the formation of a stable alloy or solid solution. The antimony (V) would then be chemically reduced with potassium iodide, and analyzed in the same way as described above.

A final specific example within this category of chemical separation is the application of a sequential extraction scheme to solid samples. Tessier et al. developed a scheme and applied it first to a sample of river sediments, and was also applied to street dusts and roadside soils by Harrison et al. The sequential extraction consisted of separating some 6 trace metals (as well as iron and manganese) into five different fractions: (1) exchangeable metals (those adsorbed to sediments and extracted by changing ionic strength in a magnesium chloride solution); (2) the carbonate fraction (for those associated with sediment carbonates, and extracted by a subsequent change in pH); (3) those bound to iron and manganese oxides (which are excellent scavengers for trace metals, and the separation was accomplished by completely dissolving the iron oxides); (4) those bound to organic matter, especially humic and fulvic acids (where trace elements were released by degrading the organic matter under oxidizing conditions); (5) and residual (which was digested in a HF-perchloric acid mixture). The resulting fractions from the sequential separation were analyzed by AAS (and/or differential pulse ASV) and also with x-ray diffraction (XDF). Although the scheme was not entirely specific it was reported to reveal a considerable amount of information concerning the metals' mobilities and bioavailabilities.
It has been pointed out that waterways, and the sea, are natural sinks for most of the environmental contaminants. An excellent review on speciation of trace metals in waters has been published by Florence.\textsuperscript{35} He pointed out that if a direct speciation analysis could not be performed, then prior separation using ion exchange chromatography was preferable over solvent extraction procedures, because it is less prone to contamination. He also pointed out the important role that humic acids play in the adsorption of trace metals in waters, especially as they usually coat iron oxide and clay particles. He also noted the important effect that pH has on the adsorption phenomenon.

C2. Instrumental Methods and Technique Coupling.

The ideal procedure for separation is a direct sample analysis but this is very challenging especially when the total metal concentrations are low in the first place. A general overview of available instrumental techniques, follows in which we shall exclude any that use thermal degradation for metal speciation.

(a) Anodic Stripping Voltametry.

One such method is that of anodic stripping voltammetry (ASV) which allows to perform some speciation and is mostly being used for speciating metals in natural water samples. This is done on the basis of different oxidation states of the elements, described as "bound" versus "free" metal (or "ASV-labile" metal.) Differential pulse-ASV (DPASV) has lower detection limits but is sometimes subject to problems like being sensitive to substances affecting the rate of reaction at the electrode, and/or peak height and peak potential.\textsuperscript{36-38} Another problem
associated with this high frequency method is the production of tensammetric waves$^{37}$, which are the result of adsorption-desorption processes at the mercury electrode that can be mistaken for metal ion waves. Some workers have used DPASV keeping the pH of the solution constant (while still removing dissolved oxygen), and were able to speciate metals in water samples at their natural pH.$^{39}$

Other commonly used methods for water samples include ultrafiltration and dialysis but both suffer from metal contamination and metal adsorption on the surfaces.$^{35}$ Bioassaying, which was previously mentioned, is another well used technique but is time consuming and somewhat restrictive to the species under observation. Ion selective electrodes, gel chromatography and radiotracers have also been used in speciation but are not widely used.

(b) X-ray techniques.

X-ray diffraction (XRD) is a powerful tool for the identification of various metals. It has been used in the analysis of air particulates samples$^{40,41}$, and soil samples. Birks$^{42}$ described the advances made in material characterizations using XRD and XRF combined. Although standard X-ray absorption does not easily lend itself for speciation, some have successfully used 'extended x-ray absorption fine structure', with an intense source for metal speciation analyses$^{43}$. Simultaneously they measured the fluorescence intensity of the characteristic x-rays to make quantitative analysis.

(c) Chromatography.

Liquid chromatography ion, exchange and gas chromatography have
been extensively used in the determination of chemical form of metals. Paper chromatography has also been used for some metals using polyphenolic compounds as spray reagents\textsuperscript{44}.

(1) **Liquid chromatography (LC):** this approach has been coupled with several other techniques and in many cases specifically for metal determination. Flame atomic absorption (LC-FAAS) has successfully been used for the direct determination of five tetraalkyl lead compounds in gasoline samples.\textsuperscript{45} The use of HPLC-AAS has been reported in the speciation of the inorganic salts of arsenic, as well as organic arsenic compounds in soils and drinking water.\textsuperscript{46,47} The same approach was used for the determination of inorganic cobalt from vitamin B\textsubscript{12}.\textsuperscript{48}

In a few cases however, stable organometallic complexes do not fully decompose. Also some metals form carbides with the graphite in the atomic absorption furnaces. Some of these interferences have been reduced by changing the furnace, or the furnace surface, or by adding a matrix modifier. Such was the case in a study with selenium in which divalent nickel was added as a modifier.\textsuperscript{49} The addition of nickel decreased the volatility of the analyte and was thought to form a nickel-selenide which also enhanced the signal\textsuperscript{50}. In one study organolead compounds were determined by HPLC-AAS in which the separated fractions were reduced by iodine and subsequently analyzed by the non-flame AAS. In another study organotin compounds were also determined in which the separated fractions were fed, in a pulsed mode, directly into a zirconium coated graphite tube.\textsuperscript{51}

Atomic emission LC is another versatile technique. A feasibility study using some 25 elements was quite successful using HPLC-ICP (argon plasma)\textsuperscript{52}. Another example of the use of emission as a metal detector
in LC was that in which gel permeation HPLC-ICP was used to speciate and conduct elemental analyses on several samples, including vitamin B\textsubscript{12}, and several proteins.\textsuperscript{53} Taylor et al.\textsuperscript{54} also used ICP as a detector in the analysis of organometallic compounds found in solvent refined coal. Their system consisted of separating nine fractions from the sample by selective elution solvent chromatography. Subsequently, 15 metals were monitored by plasma emission at the end of a size exclusion column coupled to the ICP.

(2) Ion exchange chromatography (IEC): this approach is especially well suited for trace metal speciation in natural waters, because the analyses can be carried out with little manipulations. Van Loon et al.\textsuperscript{55}, and Naranjit\textsuperscript{56}, have coupled IEC with AAS for the determination of chromium in air and water samples. Other examples of speciation studies using IEC are given and referenced in a review by Florence\textsuperscript{35}. He also included some applications of metal speciation to the study of the transfer of heavy metals across biological membranes.

Others have used IEC-AAS to speciate, the now familiar, inorganic and organo-arsenicals\textsuperscript{57}. The authors also pointed out other diverse detection systems which have been used for this purpose. In a similar fashion, Hester\textsuperscript{58} applied IEC-AAS to the analysis of arsenicals in an extract of filtered air particulates; in both of these procedures the effluent of the chromatograph was continually mixed with the appropriate reagents for the production of the respective arsines, which were then scrubbed from the solution and carried by argon into a quartz cell, which was heated to 800\textdegree C, where the atomic absorption was carried out.

(3) Gas chromatography: this form of chromatography has also been coupled with other methods for the speciation of metals. The most
commonly used have been atomic absorption and emission. The use of gamma-ray spectroscopy has also been proposed, an example of which includes its application for the development of preparative speciation of radionuclides (at temperatures of up to 1100°K).\textsuperscript{59}

An example of GC-emission spectroscopy using a helium microwave emission is that reported by Quimby et al\textsuperscript{60} in which halides, and several other elements, were selectively detected. In their system they incorporated a high temperature valve to vent the solvent, thus preventing the plasma from being extinguished by it.

A similar study involving a dozen or so elements in water samples was done by Hobbs et al.\textsuperscript{61} Others have also used spark emission to speciate metal complexes.\textsuperscript{61a}

Many applications of GC-AAS are found in literature and have mostly been used to speciate volatile organometallic compounds. Some examples include studies in which tetraalkyl lead was determined in water and homogenized fish samples\textsuperscript{62}, in sea water\textsuperscript{63,64}, as well as in gasoline\textsuperscript{65} and air samples.\textsuperscript{66,67} Speciation studies are also under way with mercury in biological fluids, the results of which have not been published yet.\textsuperscript{68} A study of butyltin\textsuperscript{60}, and manganese in air has also been reported using GC-AAS.\textsuperscript{70} (Manganese is used as an anti-knock gasoline additive.)

A general review concerning metal specific detectors in chromatography (GC and LC) has also been published by Van Loon\textsuperscript{71,72}, in which he primarily looks at atomic absorption, fluorescence and emission (microwave plasma emission) as detection systems. Veening and Willeford\textsuperscript{73} also review the applications of chromatography in the separation and determination of metal coordination complexes and
organometallic compounds, with HPLC in particular.

A somewhat extensive recent review of gas chromatography applied to organometallic compounds has also been published by Crompton. In it he assembled the information by groups of the periodic table.

(d) Mass spectrometry: this method has mostly been used with organic compounds especially when coupled to a GC, but its use for organometallic compound identification is growing rapidly. The advent of MS-MS as well as Fourier transform MS has changed the scope of MS applications by enhancing selectivity thus enabling elucidation of the structure of large and complex molecules. Sensitivities have also improved, especially with FTMS, and the few applications reported thus far, have consisted of coupling these MS units to techniques using thermal degradation of the sample.

(e) Other techniques. ESCA, SEM, SIMS and XPS (usually needing high vacuum) will not be reviewed here, eventhough they are extremely valuable in the characterization of metals on surfaces or at shallow depths.

All the examples given thus far have not included speciation using thermal decomposition in which the sample is heated and the evolved gases analyzed. This will be considered next.

C3. Speciation by thermal degradation.

Thermal analysis became important in the late nineteen forties and early fifties, but it has only been in the last decade or so that the most growth has taken place. Thermogravimetry (TGA), is the technique of probably the greatest importance in thermal analysis. It can provide information concerning the thermal stability of a compound as well as
information on the composition of pyrolysis intermediates and final product(s). Differential thermal analysis (DTA) has also been extensively used and also provides much useful information. However, because they lack sensitivity these techniques are not applicable in the determination of metals at trace levels. A derivatograph devised for simultaneously recording thermoanalytical measurements\textsuperscript{75} was successful in determining inorganic decomposition gases such as chlorine, carbon dioxide, sulfur dioxide, ammonia, hydrochloric acid and water. Still, the sensitivity using this approach did not reach ppm levels. (In this system they had managed to simultaneously measure DTA, T, TG, differential TG, thermal dilatometry and its derivative, thermogas titrimetry and its derivative). This equipment was also used to analyze the thermal decomposition products of other inorganic salts, and metal complexes. The major shortcoming of standard thermoanalytical techniques is that they measure only mg quantities, with the exception of micro-DTA instrumentation, described by Maziere\textsuperscript{76}.

The analysis of evolved gases (EGA) has also been accomplished with the use of high resolution mass spectroscopy, and more recently with fourier transform mass spectrometry. An example of the use of MS was the study of the decomposition of inorganic salts, metal complexes, geological samples, surface coatings\textsuperscript{77}.

Another approach in the analysis of evolved gases is using infrared spectroscopy whether with a non-dispersive system, or band pass filters, dispersive spectrometers or fourier transform. For the most part, the samples analyzed by EGA-MS or EGA-IR have been limited to trace organic pollutants, sample impurities, soils samples or metals and alloys. They have not included speciation of the trace metals. The primary reason
for this has been the fact that the sensitivities have been inadequate, with the possible exceptions of FTIR and FTMS.

The speciation of metals in inorganic compounds by instrumental analysis has lagged far behind that of organic samples. One of the major difficulties has been the inability of available equipment to handle the hot and often reactive and corrosive gases produced. An added difficulty has been the provision for the necessary sensitivity. As far as chromatography is concerned, columns and stationary phases still have to be developed which are able to handle high temperatures, and at the same time being non reactive. A mobile phase has also to be carefully chosen so that it can be non reactive with the analytes at the higher temperatures.

In a recent publication Bachmann reviewed the formation of volatile compounds by metals from solid samples. The author noted that for temperatures below 1000°C there exists instrumentation capable of separating many metals once they have been volatilized. They tabulated many examples. The underlying method is the formation of metal halides, hydrides, aluminum trichloride complexes or metal carbonyls, and also some volatile metal oxides, as well as reducing the compounds to their elemental form. The detection systems which have been used for these inorganic compound gas chromatography procedures include the electron capture, thermal conductivity, radioactivity detectors, flame ionization, hydride formation with their subsequent determination, electric conductivity,... An example of separation by halide formation was described by Hamm and Bachmann for zirconium and hafnium.

Even at these mid-range temperatures much care has to be taken with the equipment. As a result mass spectrometry has not been extensively
used, especially in the on-line mode. X-ray fluorescence, likewise, is best able to produce good results if the separated fractions are collected first. The methods which so far have lent themselves the best as specific metal detection systems are atomic absorption, emission and, to a much smaller extent, atomic fluorescence.

Metal speciation by thermal degradation could be classified into three broad categories: (a) non speciated total elemental analysis in which the temperature at which a signal appears reveals something about the original species involved, using for the most part non flame AAS. (b) a system in which the volatilization and detection steps are completely separated; and (c) one in which the volatilization and atomization are separated yet forming 'one unit' in which the temperature of either is controlled separately.

(a) Total elemental analysis (non-speciated).

It is interesting to note that because AAS suffers from chemical interferences (in the presence of various oxyanions for instance) many workers have been studying the processes involved in the volatilization and atomization steps of atomic absorption. The purpose was to render the technique more sensitive and simple. Chakrabarti et al. 80 recently reported of an approach which was virtually free from matrix interference. They used a graphite furnace AAS system, with capacitive discharge heating: heating is so fast that atomization takes place instantaneously.

It has been known for some time that the atomization of a metal depends to a large extent upon the original species of the compound: for example, it is well documented that halides are more volative than other inorganic salts for a large number of metals. Much useful
information for metal speciation has resulted from the studies of the
effect of several parameters on volatilization mechanisms. Some such
parameters include matrix modifiers, furnace surfaces and geometries,
gases present and evolved in the atomizers and, heating rates. Among
the data which has been obtained, the most useful to speciation have
been the appearance temperatures ($T_{\text{app}}$) of many inorganic compounds
(temperatures at which atomization is reported to begin).

Some examples of these studies in which a direct analyses was used
include the effects that adsorbed oxygen on carbon furnaces had on the
atomization mechanism (or $T_{\text{app}}$) of metal salts by Salmon et al. $^{81,82}$
Sire and Voinovitch$^{83}$ have also studied some of these mechanisms by
combining AAS with thermogravimetry, oscilloscopy and electron
microscopy. (They looked at the effects that different drying and
ashing procedures had on $T_{\text{app}}$ and signal amplitudes for several metal
salts.) Sturgeon et al. have also proposed mechanisms for compound
dissociation and metal atomization processes occuring in a carbon
furnace.$^{84}$ They deduced the information by plotting temperature
against absorption, and extrapolating energies of activation for each
reaction they were considering, such as the dissociation of a molecule
in the gas phase, for example. In another study, Czobik and Matousek$^{85}$
also have closely observed the interference effects that several
compounds had on each other, at different concentrations, and also tried
to decrease them with matrix modifiers. Other results include those
obtained by Tasuda and Kakiyama$^{86}$ when they looked at decomposition
patterns (as absorbance versus temperature) of lead, cadmium and zinc
salts in a carbon furnace using a deuterium lamp.

Ohta and Suzuki$^{87-89}$ have looked at the volatilization and
atomization temperature characteristics of some metal salts in metallic atomizers (Mo and W) and noticed them to be different than those observed in carbon furnaces. Similarly, Cantle and West used a tungsten filament atomizer to examine the temperatures at which metals volatilized. Aggett and Sprott used a tantalum strip atomizer for the same purpose and like Ohta and Suzuki, their results also differed with those obtained from graphite furnaces. West et al. also have looked at decomposition of metal salts from a W-Re (3%) wire loop atomizer.

Numerous other publications exist in which various metal and nonmetal atomizers have been used but the volatilization and atomization mechanisms were not being studied as closely as the above mentioned cases. In most instances they were only looking at the total analysis of metals and were primarily concerned with optimizing the amplitude of the observed signal. In a good number of the cases previously mentioned very fast response equipment was necessary to observe the desired signals. In many instances then, results which are pertinent to metal speciation has been provided, and it could be said that it was done so, indirectly.

(b) Trapping separated fractions.

One approach which can be used is that of having one system which separates the sample into fractions and requiring that these fractions be individually collected. Subsequently, these are also individually analysed with a separate system.

Some of Bachmann's metal speciation work falls into this category (unpublished studies of with arsenic). The procedure involved collecting "speciated products" for subsequent determination. This approach allowed one to perform several separation and collection cycles.
before the final analysis was carried out. The concept is not new and
the major drawback arises from any sample handling, increasing the
likelihood of sample or product(s) contamination.

A system of this nature lends itself well for the use of reactive
gases during the slow heating program for volatilization and/or
separation of species. But, this concept would not necessarily be
unique to a system classified in this category. This area of high
temperature separation has not been explored by many yet.

(c) On-line systems.

In contrast to the above category there are many systems in which
the separated fractions enter directly into the second part of the
instrument where the analysis takes place. Thus, the interface of these
systems designed to separate and analyze directly can be very intricate.

In this category several different approaches will be discussed,
however, the total number is still rather small.

Styris and Kaye93 have coupled an electrothermal atomic absorption
furnace to a mass spectrometer and have followed the mechanism of
atomization of vanadium pentoxide from both heated tantalum and vitreous
graphite atomizers. This technique could however, be extended to
further speciation analyzes. Similarly, Kantor et al.94 have used a
graphite (and tantalum cup) furnace AAS-flame AAS system to look at
interference studies, and speciation, mostly of inorganic zinc
compounds.

In other approaches, Robinson et al.95 have used a platinum wire-
quartz-T AAS system to look at potential speciation capabilities, mostly
with cadmium salts. The platinum wire was independently heated in this
system and the evolved gases were drawn directly onto the hot quartz-T
carbon atomization bed. This procedure was also used for a mercury speciation study.\textsuperscript{96} The system could not be heated to more than 1500°C because of the platinum, and the quartz, softening at slightly higher temperatures. Several inorganic salts of mercury were thermally decomposed and analyzed in the latter study which also included using a Hg-EDTA complex and L-cysteine bound metal (as a protein model). Because the samples were very easily volatilized (at relatively low temperatures) these results were compared to those obtained by simply placing the same samples on a glass rod, which when lowered into the atomization chamber was heated, convectively and radiatively, by the hot atomizer carbon bed. Only approximate temperature values could be assigned to the respective signals (especially below 700°C) because of equipment limitations: a good number of peaks appeared soon after introducing the samples on the top portion of the atomizer, where rapid convective and radiative heating made temperature estimation difficult. Significant "time" differences (translating into temperature differences) were observed which will provide a good basis for further detailed studies.

Other authors have used a helium microwave-induced plasma as a atomization system for the determination of evolving gases from a heated sample. Bauer and Natusch\textsuperscript{97} utilized this approach to identify and measure, semiquantitatively, the carbonate fraction of coal in fly ash. The samples were gradually heated in an induction furnace (up to 990°C) and the evolved gases carried to the plasma detection system by He. The results were quite encouraging as the signals were correlated to a series of separately analyzed, common inorganic carbonate salts. However, as the authors themselves admitted, much improvements are
required of the system to produce better resolved signals for the proper identification of the evolved gases. Another application that the authors have reported with their system is that of a more general type of study\textsuperscript{98}. In it, they looked at the decomposition characteristics of cadmium, mercury, lead and zinc inorganic salts by monitoring both the metallic emission lines as well as the anionic elemental lines. Very interesting correlations based on signal "appearance time" for the metals and non metals were made. They also postulated some vaporization mechanisms for inorganic salts based on their results. Several of the problems they encountered with their system include the furnace to plasma transfer line, the low furnace maximum temperature and its heating rate control, and sample container reactivities. Other problems involving the samples themselves were mentioned, such as reaction between the different components present within the samples, the sample size and thickness, and homogeneity.

Ohta et al. used high temperature GC-AAS to measure some atom vapor diffusion coefficients\textsuperscript{99} as well as preliminary attempts at metal speciation\textsuperscript{100}. In this procedure they measured the "appearance times" of copper and manganese nitrates, and magnesium and sodium chlorides, in a ten inch molybdenum tube (which also served as atomizer). The column could be heated in different sections to different temperatures, and the atomization portion up to 2200°C. They also observed the effect of hydrogen on the relative metal "appearance times" when it was added to the argon carrier gas. (Other parameters that they were going to study as well, were samples having heavy matrices like seawater, biological and other environmental samples.)

A short time before these approaches were reported, a similar
concept was used in these laboratories when Robinson and Rhodes$^{101}$ used a two stage atomizer system to look at the potential that such an instrument would have for metal speciation. Their procedure involved placing a sample in the volatilization section while the separate atomization section was hot. The first section was then gradually heated up to 2000°C, for example. As gases evolved from the sample they were carried through to the hot atomization section, where the atomic absorption took place and the signal recorded. Standard compounds were first analyzed before any complex samples were used. Thermal-AAS curves of individual lead and cadmium inorganic salts were recorded. They were subsequently able to speciate, though rudimentarily, complexed and uncomplexed metal from solutions in which EDTA complexes had been formed. The sensitivities obtained using 1000 ppm metal concentrations were far from those needed for trace level measurements. These were improved when the graphite analyzing sections were replaced with molybdenum tubes because the former were found to become somewhat porous with use creating reproducibility and sensitivity problems. A slight modification to the metal atomization section allowed for still slightly better sensitivities as well as some precision improvements: the diameter of the hole through which the gases entered this section was reduced. In this configuration they were also able to observe four different broad signals for a sample of tetraethyl lead in artificial sea water.

D.-Two Stage Atomizer.

A closer look at the parameters involved in the system mentioned
above was required before any significant improvement could be accomplished.

The work presented in this dissertation had several purposes: (a) the continuation of the feasibility study which had just begun, in particular, with the analysis of inorganic compounds; (b) the control of procedural parameters such as precise temperature measurements, sample injection precision, heating and flow rates. These parameters drastically affected sensitivity, precision and signal resolution; and (c) the introduction of minor alterations and modifications to the instrument, with their continuous evaluation. In order to simplify the assembly and improve the system's performance a "second generation atomizer was later designed. (Modifications and alterations to the atomizer took second place to the other two aspects, partly because of the relatively limited resources available for instrumental development, and partly because of the length of time that is required for instrument design.)

D1. Temperature Control.

The control of procedural parameters was of primary importance and the accurate measurement of temperatures proved to one of the most difficult tasks.

High temperature measurements require rather extensive calibration procedures. Some have used thermocouples, but these are not commonly used above about 1500°C; photodiodes have also been used but these are better suited for mid to high temperature ranges, as are optical pyrometers, which have been used as well: both of these depend on emitted radiation. Some commercial instruments sense the current flowing through a carbon furnace for instance, and a corresponding
voltage signal is sent to the "temperature meter", having previously been calibrated to read in degrees C or F. However, the latter systems are highly dependent on the condition of the (graphite) furnaces. As a result, the preparation of temperature working curves have been essential and only accomplished by the careful measurements of furnace temperatures. These, then, need to be correlated to either electrical current, infrared or visible radiation, voltage or to some other means. The approach which was chosen for our studies was that of placing a chromel-alumel thermocouple near the furnace, at the place where it got the hottest. Calibration in this position was accomplished with an optical pyrometer for the higher temperatures, and with another thermocouple placed inside the vaporization section for the lower temperatures. This system proved adequate for the present studies.

D2. Carrier gas flow rate.

Another procedural parameter which also needed evaluating was the flow of carrier gas going through the tubes.

The concept of speciation as a function of temperature rests on the ability to resolve the signals produced by the evolved gases. The flow rate of the carrier gas would then be very important.

D3. Heating rate.

The resolution of the signals also depends considerably on the applied heating rate, again paralleling furnace temperatures in programmed temperature gc.

D4. Sample introduction.

The reproducibility of the observed signals depended on where the sample was placed within the vaporization section. This was particularly so because the metal analyzing section when heated exhibited a rather
marked temperature gradient along its length. This was the result of the water cooled connecting brass electrodes at each end. Thus, it was very important that the sample be consistently placed in the portion of the tube which would get the hottest.

**D5. Distance between analyzing sections.**

Another quite important consideration was the distance that existed between the two analyzing sections. As the sample was gradually heated the evolved gases were carried by the argon carrier gas toward the atomization section. This metal piece was smaller in diameter than the vaporization piece and consequently there would be a partial accumulation effect. The distance between the two sections was therefore important because it provided a place for evolved gases to condense, especially if the temperature there was lower than that of the gases. The size of the common carbon center electrode controlled this temperature to a large extent in part, because its ends were in contact with water cooled brass electrodes. Thus, high enough temperatures between the analyzing section were necessary so that the gases would not condense.

It was also necessary to correlate the thermal degradation results obtained for each compound with those from plausible decomposition mechanisms: in some cases more than one peak was observed for each compound, particularly with halides.

As far as instrument modifications were concerned, several were introduced in an attempt to primarily alleviate the task of assembling the system; other improvements were also brought about. Thus, further evaluation of a two stage electrothermal atomizer for metal speciation was accomplished by looking at several samples.
2. **EXPERIMENTAL: CHEMICALS, EQUIPMENT AND PROCEDURES**

2A. CHEMICALS.

Generally inorganic salts used were commercial regent reagent grade with a few exceptions listed below. (Suppliers included Mallinckrodt, Baker, Merck, Matheson Coleman and Bell, Allied Chemical, Fischer Scientific, City Chemical.)

*Lead Oxide:* or red lead was prepared by slowly roasting lead monoxide below 500°C;

*Lead Chromate:* was prepared from a solution of lead nitrate in which sodium chromate was added;

*Lead molybdate:* was precipitated from a nitrate solution and sodium molybdate. All solutions were kept in polyethylene flip top vials.

Hydrochloric acid and furfuryl alcohol, which were used for polymerization of carbon, are also commercially available.

2B. EQUIPMENT

Because of the nature of the experimental system that was used, the apparatus itself and its operation are described in two different sections: Equipment and Procedures, respectively. A parallel sub classification within these two sections was attempted because the first describes the system very briefly, whereas the second explains in greater detail the procedures used to operate the instrumentation, as well as the construction and modifications of the various components.


(a) *Hollow Cathode Lamp:* the instrument bracket which holds the hollow cathode lamp (HCL) was modified to accommodate a demountable
HCL. These light sources have been used in these laboratories for quite some time and their operation, as well as the construction of the lamps, have been detailed before \(^{102}\) (Figure 1). However, because it is smaller in diameter than a commercial sealed hollow cathode, spacers were placed and adjusted on the lamp bracket so that a maximum amount of light reached the detector. In addition, two half inch holes were punched through the top of the bracket for accessibility of the lamp's electrode connection, from which electrical leads plugged into the receptacle on the bracket.

(b) **Deuterium Lamp and Power Supply:** the instrument's deuterium lamp was replaced with a Beckman D\(_2\) lamp, No. 6280 which was incompatible with the PE D\(_2\) Arc Power Supply. Therefore a Beckman H\(_2\) lamp Power Supply, model B compatible with the lamp was used.

(c) **Perkin Elmer D\(_2\) Power Supply:** a couple of modifications to the PE D\(_2\) Arc Power Supply were necessary in order to actuate the reference beam shutter on the PE-403, and the neutral density filter wheel which adjusts the intensity of the deuterium lamp reaching the detector. A high wattage resistor was substituted for the D\(_2\) lamp and the ballast lamps on the power supply were removed and replaced with a single 7 1/2 watt bulb. Otherwise the beam attenuator solenoid would burn up.

(d) **Kymograph:** the normal heating program provided by this unit was not used because a slower heating rate was necessary. A temperature ramp accessory for an HGA-2000 unit is available from Perkin Elmer but was expensive, therefore a less sophisticated approach was used. The shaft of the kymograph (Phillips and Bird, Inc., having five speeds), was connected directly to the shaft of the atomizing
EXPLODED VIEW OF A DEMOUNTABLE HOLLOW CATHODE

Figure 1
temperature control on the HGA unit by a short piece of, thick walled, tygon tubing. Because of the clockwise rotation of the kymograph shaft, and also because this unit was going to face the HGA, the electrical leads to the temperature control potentiometer were reversed so that the temperature of the furnace could be gradually increased with the kymograph, at any of its five speeds.

(e) **Temperature Switch**: an on-off switch was added in parallel with the atomizing temperature control button. Heating the furnace was done with it in the on position.

(f) **Temperature Signal**: the HGA temperature meter was calibrated by the manufacturer as a function of the current that passes through the graphite furnace to read temperature directly. The temperature sensor of the furnace produces a voltage proportional to this current and is displayed as temperature. A circuit was built so that this same voltage could be supplied to the recorder in order to monitor the temperature of the furnace, continuously, without effecting the reading on the HGA meter.

(g) **Furnace Window Housing**: the furnace assembly did not include end windows, therefore, to keep air away from the carbon tube a high purge gas flow rate was required. Later models have come equipped with adaptators to them which remove this deficiency. The window housings produced by the Chemistry and Physics Machine Shop were designed in the past by previous workers in the group and made of teflon. These were attached to the furnace's high current contact plates. At the ends of each, the quartz windows were secured with threaded rings, and the fittings for the gas inlet were about an inch from the ends. As a result a much lower purge gas flow was needed.
(h) **Purge Gas Flow:** high flow rates of nitrogen can suitably be adjusted with the flowmeter built into the HGA. However, because of the window housing additions lower nitrogen flow rates needed to be properly measured. A Matheson #601 flowmeter was introduced between the HGA unit and the furnace for this purpose.

1. **Recorder:** a Texas Instrument dual overlapping pen servo/riter II recorder having a span of 1 mv was used.

   1. **Recording the absorption signal:** the recorder was fitted with a ten turn, 20 K ohm potentiometer to receive the signal from the 403 atomic absorption unit.

   2. **Recording the furnace temperature:** the signal provided by the added circuit to the HGA was connected to a ten turn, 200 ohm potentiometer, having a 33K ohm resistance in series.

   **Syringes for sample introduction:** liquid samples were introduced into the furnace either with a 1-5 microliter adjustable Finnpipette or with a 10 microliter Hamilton syringe. (A small length of teflon tubing fitted onto the two inch needle of this syringe did not prove to be any more advantageous than injecting samples without it, as far as contamination is concerned).

   Solid samples, i.e., sections of glass fiber filters, were placed inside of a disposable pipet which was introduced in the vaporisation tube. The disposable pipet had a nichrome wire of the appropriate size as a plunger.

2B, 2. **TWO-STAGE ATOMIZER UNIT.**

The essential components of this atomizer system are schematically
shown in figure 2. The diagram does not include any of the associated equipment required for AAS since these will be detailed individually.

![Diagram of the Two-Stage Atomizer](image)

**Figure 2**

Diagram of the Two-Stage Atomizer

(a) **Optical Beam and Signal Processing System.**

(1) **Hollow cathode lamp**: See figure 1, also reference 102.

(2) **HCL power supply**: Tecktron AA-3 spectrophotometer hollow cathode power supply, type MCS-1, 450 v max., 3-50 ma dc.

(3) **Deuterium lamp and power supply**: Beckman lamp No. 6280, and Beckmann H₂ lamp power supply, model B.

(4) **Light source modulation**: A .002 hp motor (1800 rpm) was used as a chopper. The blades activated a reed switch which was mounted
on a adjusting wheel made in our laboratories. The reed switch signal was sent to the amplifier and was the reference signal for the phase sensitive detector. The wheel could be rotated 360° about its axis and was used to maximize the signal of the amplifier once the source and chopper were set in position. (Signal phase adjusting.)

(5) **Monochromator and detector:** a Jarrell-Ash 0.5 m (model 82-000) Ebert monochromator was used. It had a 1180 lines/mm grating and exchangeable fixed slits (entrance 100 μm and exit 25 μm). The resolution with the given exit slit width was 0.4 mm in first order. The detector was a Hamamatsu photomultiplier tube (PMT), No. R106. Voltage supplied to the PMT came from an Hewlett-Packard, model 6515, 0-1600 V, 0-5 ma d.c. power supply. Between these two was a junction, or adaptor box having a 1 Mohm, protective resistance on the BNC connection. (The MHV input of the power supply went to the octal connector, to the PMT, and back through the octal connector, and then through the 1 Mohm resistor and BNC connector; the amplifier was connected to the BNC end.) In this system, however, the junction box was not really necessary since the amplifier used was designed to receive the PMT anodic current directly.

(6) **Amplifier:** a GCA-McPherson/Heath Photometric readout amplifier, model EU 703-31 was used. It has been modified to operate in a phase locked mode with an external chopper (60 Hz). The 1 volt output to the recorder was used.

(7) **Recorder:** Beckman 10 inch lab potentiometric strip chart recorder. Part of the signal from the amplifier was fed into the recorder, since it was operated at the 100 mv linear span.

(8) **Timer:** Standard Electric Time Co., type S-60, one rpm
timer. This timer was used to gradually heat the atomizer at regular time intervals.

(b) **Atomizer and Components**

1. **Molybdenum pieces:** the atomizer analyzing sections which were heated to high temperatures were made out of this metal. All Mo pieces were machined by the Chemistry and Physics Machine Shop, out of a 1/4" diameter rod.

   (a) **Vaporization Section:** all sections used were essentially a tube of ca. 1 3/8" in length having a wall thickness of ca. 0.023". Figure 3 shows the two basic designs and dimensions which were used in these studies.

   ![Figure 3](image)

   **Figure 3**

   Molybdenum Vaporization Sections
   (a) initial design; (b) latter design.

   (b) **Atomization section:** the evolution of the different designs and dimensions for this molybdenum section are depicted in figure 4. The first two were not used in this study, but only in previous work done in this laboratory.
Figure 4

Evolution of the Molybdenum Atomization Section. (a) is essentially a tube; (b) incorporates a constriction at the entrance thus improving sensitivities; (c) extends this constriction, becoming the atomization channel; (d) incorporates a cup at the atomization channel end in order to decrease its fragility; (e) incorporates a taper on the cup to increase the contact area; (f) the optical path is brought nearer the atomization channel to simplify machining.
The optical path was the hole drilled across the rod and ranged in diameter from 11/64 to 3/16", which produced the approximate corresponding volumes of 0.056 to 0.067 cubic inches (0.095 to 0.11 cc, respectively).

The wall thicknesses throughout these pieces were kept close to 0.023" so that heating could be as uniform as possible.

The atomization channel, the narrowest portion of the piece, had an i.d. of 5/64" and an appropriate o.d. (ca. 0.120") to accommodate the approximate wall thickness mentioned above.

The end-portion of the metal piece (on the opposite end from the optical path), at first was the same size as the atomization channel (figure 4c). The connection to the carbon center electrode with this design was delicate, especially after a few heating cycles. Changing the end portion to a 1/4" cup added sufficient rigidity for a better molybdenum-carbon electrode connection. The length of this end-portion varied from 0.2 to 0.15", and was 1/4" o.d. (figure 4d).

(2) Carbon pieces: the molybdenum pieces were not connected directly to the outside brass electrodes but rather to carbon pieces which served as supports. The first design of this double stage atomizer used carbon sections rather than molybdenum and previous experience with atomizer designs dictated the necessity of having carbon supports. All of the carbon pieces were machined from Ultra Carbon Corp rods by the author.

(a) Center Electrode: each molybdenum piece was connected to a common center electrode made of carbon, which in turn was connected at each end to separately water-cooled brass electrodes. Figure 5 shows the different configurations of this center carbon electrode which were
(a) one large and small contact

(b) two contact joined by narrow hole

molybdenum

(c) larger electrode to reduce resistance

(d) single hole for both contact

(e) tapered contact holes for better contact

Figure 5

Differences in the Various Center Carbon Electrodes.
tried. The first variation was used with the first design of the molybdenum atomizer section (having the long and narrow atomization channel, as shown in figure 4c). Another three were used with the next atomization section design (shown in figure 4d). Finally, the last diagram in figure 5 shows a slightly expanded diagram of the carbon center electrode that was used to accommodate the tapered ends of the last two metal pieces (shown in figure 4e,f) The center hole of this last carbon piece was drilled to appropriate depths using a drill bit which had a tip which matched the taper on the molybdenum pieces.

The tapered ends of the last two carbon pieces of figure 5 were different due to changes introduced to the brass electrodes (detailed later); these differences are not depicted in the diagram however.

(b) Front and Back Carbon Supports: all carbon used for this purpose was machined from one inch rods and were, on the average, about one inch long. Figure 6 shows the several features of these carbon

![Diagram of the Carbon Supports Used in the First and Second Atomizer.](image)

Tapers gave better electrical contact.
supports, including the similarities, and small differences, between the front and back pieces; also, the geometry differences brought about by the design change of the brass electrodes going from the first to the second atomizer.

The front and back carbon supports were essentially the same, particularly at the very beginning, using the first generation of the atomizer. The argon flowing through the molybdenum pieces was exhausted through the center of the back carbon support and brass electrode. Subsequently, it was decided to funnel this flow through the exhaust port of the atomizer body. Therefore, henceforth it was not necessary to drill the carbon piece all the way through, as the front one was, but only deep enough for the metal piece connection.

For a period of time copper was electro-deposited on the surface of all the carbon pieces which were in contact with the brass electrodes. The purpose of this was to decrease the voltage drop occurring at these interfaces by increasing the conductivity of the carbon at their surfaces.

(3) Electrical system: the two molybdenum analyses sections were heated separately with two separate systems (120 V, 45 A lines). A diagram is shown in figure 7.

(a) Atomization Section: the power was regulated with a variac (115 V, 18 A), and an ammeter was placed before the stepdown transformer (Signal Transformer 6., 9 V, 500 A). The two isolated primary windings of the transformer were connected in series at 110 V.

(b) Vaporization Section: two 20 A ganged variacs, connected in parallel, provided the power regulation. An ammeter measured the line current being drawn. Two 12 V, 500 A stepdown transformers in
Electrical Diagram for the Two-Stage Atomizer. The variable auto transformers were used to gradually heat the vaporization section. The variac shown at the bottom of the figure, was used to control the heat provided to the atomization section.
series were used. The two isolated primary windings of each were connected in parallel.

Welding cables were used from all secondary windings to the atomizer electrodes.

(4) Gases:

Helium: helium was the filler gas in the hallow cathode. It was regulated with a needle valve and measured with a vacuum gauge (see figure 8). It was oxygen scrubbed by using heated copper turnings.

Argon: argon was the inert gas used in the atomizer and figure 8 show a diagram of the system. The flow of argon through the molybdenum analyzing tubes was controlled with a Matheson 600 flow meter.

The argon flowing directly into the body of the atomizer sewed to purge any air present, as well as to keep the system in an inert atmosphere. This flow was adjusted with a J. T. Baker 568274 flow meter.

All the argon was dried, cleaned and oxygen scrubbed by using silica gel, activated charcoal and heated copper turnings, respectively.

Methane: this gas could be mixed into either or both streams of argon. The argon flowing into the body of the atomizer was mixed with up to 1.5% methane (usually only about 5-10 cc/min), to scavenge any existing oxygen. Methane was also dried and cleaned like the argon and the flow rate regulated with a Matheson 610 rotometer.

(5) Vacuum: in the first stages of the work a diaphragm pump (Dyna-Vac Pump model 4 K, by the Cole-Palmer Instrument Co.) was used to draw argon through the analyzing sections and from that provided to the atomizer body. Presumably, all the argon and methane going into the
Figure 8

Diagram of the Gas System for the Two-Stage Atomizer. Argon was used to provide an inert atmosphere. It was dried with silical gel. Trace components were removed with activated charcoal and oxygen was removed with hot copper turnings. Separate streams entered the atomizer. Cleaned methane was only mixed with the argon going into the atomizer body.
atomizer was exhausted through the back brass electrode. The total flow rate was regulated using a Matheson 602 flow meter.

The vacuum system, also shown diagrammatically in figure 8, included a cotton wool filter between the atomizer and the flow meter. There was also a container between the flow meter and the pump which reduced suction surges from the pump.

(6) Syringes for Sample Introduction: the depth into the vaporization tube where the samples were placed required the use of a 4" long needle. Two 10 syringes with 4" removable needles were obtained: the Hamilton 701-RN syringe with a 26-S GA-B needle gauge and tip; and the Precision Sampling C-160222 syringe with the 123050, 26 gauge needles.

For the solid filter samples a piece of glass tubing was used which was long enough and had a diameter small enough to fit into the vaporization tube. The sample of filter paper was “injected” with the use of a nickrone wire as a plunger.

(7) Temperature measurement:

(a) Thermocouple: three thermocouples were used. The first, was an iron-constantan (with a gauge by Alnor, Illinois Testing Laboratories, Inc.) It served to get an indication of the temperature of the carbon center electrode. This was achieved by simply drilling a hole in the carbon, (at the same height as the molybdenum pieces) deep enough to place the thermocouple junction into the carbon. This measurement gave a good indication of the temperature in the space between both molybdenum pieces.

The other two chromel-alumel thermocouple with wires 0.032" diam each (AWG #20). One was used to monitor the vaporization section
temperature (body-TC). It was calibrated for temperatures below 1100°C with measurements obtained from another one placed within the tube itself.

The gauges used with these two thermocouples were made by Edmund Scientific Co., or Blue M Electric Co. for the first, and Thermo elec. Mfg. Co, with the second.

(b) Optical pyrometer: Leeds and Northup model 9632-C, 775-2800°C. It was also used to measure, and calibrate, the vaporization thermocouple (or body-TC) at the higher temperatures.

(c) First Atomizer Housing Design.

This first design was produced by a previous worker and has been explained in detail101,102 (having an interior volume of ca. 450 cc). Figure 9 shows a cross section diagram of the components. There were a few modifications and additions to the system which are summarized in figure 10, and they include:

1. **Tapered electrodes:** the ends of the top and bottom brass electrodes which connected to the carbon center electrode, were somewhat deteriorated and therefore modified from about a 10 to a 45 degree taper, and 3/36" deep. (Figure 10a)

2. **Top and bottom electrode holders:** the spacing of the O-ring grooves on each of the top and bottom electrodes did not allow both Viton O-rings to be contained within the bakelite insulators. When the electrodes were in place, one O-ring was within the insulator and the other was either still on the outside of the atomizer or beyond the bakelite, on the inside of the atomizer. This was due to the fact that the bakelite pieces had deteriorated to a considerable extent by the heat produced within the atomizer, but this conclusion was not reached
Exploded diagram of the components of the First Two-Stage Atomizer. A: front and back brass electrodes. B: Top and bottom brass electrodes. C: atomizer housing including the optical lightpath.
Figure 10

Modifications to the first stage atomizer (a) Reconstruction of the top and bottom brass electrodes note change of connection taper (b) holder used for top and bottom brass electrode (c) Body-thermocouple, holder and shield.
until much later in the studies. As a result the electrodes did not fit tightly against the carbon center electrode, nor did they keep air out. Therefore, a compressing system to maintain good electrical contact between the brass and carbon was devised.

Figure 10 b depicts the arrangement. Commercial packaging metal ribbon was used to make a bracket which fit over the electrode and extended on each side. Through the top of the ribbon, and centered on the top of the electrode, a hole was punched through, which was large enough for a 10.32 screw to fit. On the underside of the ribbon a corresponding nut was affixed to the screw. The tip of the screw was rounded off and made to fit a smooth, shallow and centered depression on top of a metal disc. This disc was insulated on its other side and placed on top of the electrode. The ends of the metal ribbon went under hose clamps which were tightened around the body of the atomizer, so as to anchor them. As the screw was turned while the nut was held in position, the electrode could be pressed into the atomizer providing a good electrical contact with the carbon, and maintaining it.

As tension was placed on the compressing system it was noticed that the electrodes tilted. To correct this problem a teflon sleeve was fit tightly over the portion of the top brass electrode which slid through the bakelite. This addition allowed the electrode to slide in and out without any lateral tilting. The same objective was achieved in the bottom electrode by machining a replacement bakelite insulator having a hole which provided a tight fit with the electrode.

(3) Thermocouple and holder: In order to monitor the temperature of the vaporization tube continuously, a chromel-alumel thermocouple was introduced into the atomizer through a hole drilled
into the front transite annulus of the atomizer. This hole was drilled approximately at the bottom right portion and once the thermocouple was in place, silicone rubber sealant was used to seal the hole.

The thermocouple was fixed in space near the molybdenum piece, and shielded from reflected radiative heat within the atomizer (coming from the hot atomizer section) by two pieces of transite as shown in figure 10 c. One piece of transite, the base, consisted of a rectangular rod of the proper length (about 3" long) to fit snugly within the two annular transite insulators at each end of the atomizer. A hole was drilled along its length up to a point equivalent to the center of the vaporization section. At this point another hole (1/4") was drilled normal to molybdenum piece. The shield portion was snugly fitted into this hole, and extended about half an inch from the base. The thermocouple was then threaded through the base and up through a hole drilled along the shield portion.

Because the mass of the shield was large, it was noticed that the heat which it absorbed could not easily be dissipated. Once the vaporization section was turned off, it kept the thermocouple from cooling within a reasonable period of time. As a result the transite shield portion was substituted for a piece of available steel, which was formed into the desired shape.

\[ d \] Second Atomizer Housing Design:

(1) Internal components: the arrangement of the pieces are depicted in figure 11, showing the molybdenum analyzing sections, the carbon supports and center electrode, and the approximate relative positions of the thermocouples being used.
SECOND ATOMIZER INTERIOR
COMPONENTS

All four brass electrodes were redesigned for better electrical connection and facilitating assembly. A thermocouple was added to monitor the vaporization section temperature.
The designs of the molybdenum pieces were essentially the same as those used with the first atomizer. In the latter portion of the study the ends were tapered to 82 degrees in order to increase the contact area in the connection. Figures 3e, f depict this change. The distance between the two pieces within the carbon center electrode varied from 1/16" to 3/8", and was usually not carefully controlled.

All carbon pieces were machined out of Ultra Carbon graphite rods. The supports were made out of one inch rods and the center electrode, at first, was also made out of a one inch carbon rod, but then only 3/4" rods were used. All four brass electrodes were tapered to 55°, and so all carbon pieces were machined to this taper and also drilled to 82°, for the connections with the tapered molybdenum sections.

Two thermocouples were used to measure inside temperatures. A chromel-alumel junction was positioned normal and just above the vaporization section (body-TC). The distance between this junction and the Mo tube was usually gauged with a 23 Brit. Std. gauge wire (0.024 in.), because it was convenient. The wires for this thermocouple were fed into the atomizer through a port in the aluminum housing, and were held somewhat rigidly in position by resting in a hole drilled through a square transite rod, which was cut to fit upright inside the atomizer (see figure 11).

To measure the approximate temperature of the center carbon electrode between the molybdenum pieces, an iron-constantan thermocouple was placed in a shallow hole drilled into the carbon, at the same height the metal pieces fit into it.

The thermocouple openings in the atomizer housing were sealed with
commercially available silicone rubber sealant.

(2) **Brass electrodes and connecting cables:** Some of the main considerations in the design of these electrodes included the requirement of adjusting the depth to which they would be introduced into the atomizer (therefore able to adjust to the interior components' lengths). They also had to be water cooled, durable, not expensive, good electrical conductors,.... The resulting design is depicted in figure 12 and 12A. Figure 12 shows the assembled unit and figure 12 A an exploded view of the components.

In order to adjust the depths to which they could be introduced into the atomizer three of them were threaded through 1/2" thick, threaded metal rings which were securely attached to the electrical insulators, mounted on the atomizer housing. As a consequence the welding cable end connections also had to be modified to accomodate the rotation of the electrode while the cables themselves were stationary. A 1/2" hole drilled through the end connections of the cables with a provision for a set screw solved this problem satisfactorily. To allow for carbon expansion of the carbon center electrode due to heating, the top brass electrode was spring loaded.

Electrical insulation for the atomizer housing was necessary and led to the use of a phenolic laminates (like Bakelite or Micarta). On the front and back pieces, an O-ring was included on the inside surface of the insulator providing an air seal with the brass electrodes; because even viton O-rings had decomposed in the top and bottom electrodes of the previous atomizer, it was not thought wise to place them in the same arrangement. The bottom electrode, therefore, had the O-ring on the outside surface of the threaded metal ring, parallel to
Diagram of the assembled two-stage atomizer. Not shown are the internal components.
Figure 12 - A
Brass electrodes and associated connections in the second two-stage atomizer.
the body housing, where radiative heat could not decompose it. The air
seal was made as the electrode was screwed into place. A comparable
seal could not be achieved with the top electrode because the teflon
sleeve through which it slid into the atomizer, had to provide enough
space for free slippage since it was spring loaded. All of these
components are depicted in figure 12.

All bakelite insulators were mounted to the atomizer body with
four screws each, and all common surfaces were sealed with commercially
available silicone rubber sealant.

(3) Atomizer body: The body was made of aluminum because it
was inexpensive and easily machined, although maybe not as easy to weld
as other metals might be. Figure 13 shows a sketch of the atomizer
(having an interior volume of ca 1.6 ). The main section had a water
jacket for cooling as did both sets of doors. Two openings for the
thermocouples were included, as well as two more for the argon inlet and
the gases exhausts (although positive pressure would force some argon to
escape through all existing gaps).

Each door was fastened to the body with four screws, which when
tightened would compress O-rings fitted into rectangular grooves milled
on the inside of each door. (These seals were made against the atomizer
wall.) These doors were easily removed when necessary.

On each of the doors were two circular openings. The smaller one
was for the quartz window (optical path) and the larger one was a
viewing window. The latter had an 1 1/2" diam., 1/8" thick plate glass
(obtained from a local hardware store). To reduce the amount of
radiation falling on it and causing it to crack by expansion a slitted
attenuator made of aluminium foil was placed on the inside of the
Figure 13
Exploded view of the atomizer housing, showing the doors, top and back brass electrodes, and viewing windows.
glass. Between the glass and the exterior aluminum ring retainers was a polyethylene ring to avoid glass to metal stress.

Both quartz and plate glass windows were fitted with O-rings on the inside to provide an air seal, and were also easily removed for cleaning and/or replacing.

(e) Copper Electrodeposition on Carbon.

In an attempt to decrease any voltage drop between all carbon and brass pieces it was thought that electrodepositing copper on the carbon might provide a better contact. The equipment used was simple and consisted of a variac which was connected to a power transformer. The terminals of this transformer, which provided an output of 6.3 V at 4 Amp were connected to the ac terminals of a rectifier. The rectifier in turn, provided the necessary voltage and current to deposit copper, onto the submerged carbon electrode support surface, from a copper nitrate solution. The anode was a platinum wire, in the form of a circle surrounding the carbon electrode. It was found that ca. 0.2 volts dc with ca. 400 ma provided good deposition from the magnetically stirred solution. (See Figure 14)

28,3. Air Sampling Equipment.

(a) Pump

A Dyna-Vac diaphragm pump, model 4 K from Cole Palmer Instruments Co was used to draw air through a filter, at a rate of 3-5 L/min.

(b) Filter

Gelman glass fiber, type A #61694 with a 99.9% retention for particles of 0.3 micrometer. These filters had to be cut to fit a Gelman one inch, in line filter holder (#1109)
Copper Electrodeposition System. Tip of carbon electrode was copper plated.
(c) **Flow meter**
Dwyer 0-5 l/min.

(d) **Analytical Balance**: Mettler type H5, 160 g.

2B.4. **Thermogravimetric Analysis**.

(a) **Dupont 950 Thermogravimetric Analyzer**, with nitrogen as a purge gas, and a platinum boat.

(b) **Dupont 900 Thermal Analyzer**, 0-1000°C
2C. PROCEDURES.


Stock solutions of soluble salts of 1000 ppm were prepared in distilled deionized water and kept in large flip top polyethylene vials. Saturated solutions of the less soluble salts were used, including the oxides, sulfates and some of the oxyanion salts.

2C,2. Hollow cathode preparation and operating conditions.

(a) Cadmium: the hollow cathode was prepared by melting and then drilled (7/64" diam.) the metal in a brass cup. An approximate d.c. current of 20 ma was used both with the PE-403 and double stage systems. The analytical absorption line used was the 228.8 nm, and 226.8 nm for background correction with the PMT voltage being increased to achieve the same transmitted intensity.

(b) Mercury: the cathode was made with a copper foil, or a copper tube of the proper size to fit in a brass cup and amalgamated in mercury for at least 2 or 3 days. A small dc current of 3-5 ma was used. The analytical line used was the 253.7 nm, and since the 257.6 nm non resonance line was not intense enough, the molecular background was measured with a deuterium lamp, having to increase the PMT voltage to obtain the same baseline signal.

(c) Lead: metal was melted into a brass cup and the cathode drilled (7/64" diam.) A dc current of ca. 18-25 ma was used. The 283.3 nm analytical line was used along with the non resonant 280.2 nm line for background corrections. The baseline intensities were balanced by increasing the PMT voltage or alternatively by regulating the current
and pressure of the lamp.

(d) Zinc: analytical reagent grade mossy zinc was melted into a brass cup, and drilled to 7/64" diameter. D.c. currents of 20-25 mA were used. The analytical line used was the 213.9 nm. (The deuterium lamp was used because the non resonant lines were too weak (210.4^103 or 212.5nm^104).)


All studies were performed using the deuterium background correction and in the absorbance, repeat, and 10 average mode. Other aspects of the operation of this system are detailed below.

(a) Methods of purging: originally the furnace was not equipped with quartz end-windows and the recommended procedure to keep the graphite tube under an inert atmosphere called for the use of a large purge gas flow rate, from the top of the furnace in the order of 6 l/min. The addition of end-windows permitted the reduction of the nitrogen flow rate considerably, ranging from 10 to 270 cc/min. A flow meter was then placed between the HGA unit and the furnace, and calibrated at 20 psig (soap bubble method).

Two methods of purging were tried: (i) from the windows or (ii) from the top of the furnace "toward the windows". The former arrangement proved to be preferable (the figure 15). In both flow rate approaches, however, no gas flow could be measured at the opposite end from which the gas went in, even with nitrogen flowing in at 270 cc/min. Therefore, only the flow entering the "y" separation was reported.
FLOW RATE. PbCl₂. 10 ppm

230 cc/min

130 cc/min

230 cc/min

(a) (b)

Figure 15

Methods of Purging the PE Graphite Furnace. (a) From the windows (b) From the top of the furnace "towards the windows". Best results with low trailing were observed at 230 cc/min. using (a)

(b) Flow rates: data relating the signal obtained as a function of the flow rate, at the slower heating rate, are shown in figure 16 using 5 ppm levels of lead chloride. Subsequent studies using the motorized heating mode were conducted at 130 cc/min. This provided a large enough signal over a reasonable temperature range. The flow of the gas was never interrupted during a heating cycle.

(c) Cleaning the furnace: at the outset of all work it was noticed that the background absorption was considerable even after prolonged conditioning of the graphite tube at the maximum temperature (ca. 2400-2470°C). Dismantling and cleaning the whole furnace in dilute
Absorption Traces as a Function of Purge Gas Flow Rate Using the PE Graphite Furnace. (Flow coming from the windows.) Best compromise between signal trailing and intensity was used, namely, 130 cc/min.
HCl resolved that background problem. Each new tube was conditioned by high temperature cleaning before using.

(d) **Recording of data:** the recorder speed was 0.25 in/min. The temperature signal coming from the furnace control unit was adjusted to a maximum temperature of 2300°C to be full scale on the recorder.

A neutral density filter (a wire mesh) was placed at the hollow cathode to set the absorption scale on the recorder. While the system operated with the D₂ lamp the recorder pen was adjusted with the 10 turn potentiometer on the recorder. On the PE 403 unit the zero had to be adjusted with the appropriate control.

All measurements were recorded with the smallest time constant available, namely 0.25 sec.

(e) **Sample introduction:** the adjustable Finnpipette microliter dispenser was used at first, but because it placed strain on the graphite tube at each sample introduction further use was discontinued. A 10 μl Hamilton syringe with a standard 2 inch needle was subsequently used.

All injections were made cold since better reproducibility was achieved than injecting the samples at higher temperatures (100-200°C).

(f) **Heating rates:** the effect of heating rates were studied. It was noticed that slow heating rates caused sensitivity losses. The purpose of using slower heating rates was to observe whether speciation was possible, while correcting the signal background. The instrument did not include any control over this parameter, and therefore, heated the furnace quickly to a predetermined temperature. Two approaches for the gradual heating were used.

(1) **Manual control:** the first approach was to increase
the furnace temperature by equal increments, at predetermined lengths of
time, e.g., at a rate of 100°C every 10, 15 or 20 sec. This procedure
involved adjusting the atomizing temperature potentiometer to the
indicated temperatures on the furnace meter. The push-button used to
set the atomizing temperature was kept depressed for the duration of the
heating cycle. An on-off switch later replaced having to push this
button. Figure 17 shows the effect of using this heating mode with a
sample of lead chloride. Spurious signals were more pronounced at the
slower heating rates.

Figure 18 shows a study of the signals obtained as a function of
flow rate of the nitrogen purge gas using this manual control approach.
A heating rate of 100°C/10 sec was chosen for this study. A flow rate
of about 45 cc/min produced the most intense signals and therefore was
preferentially used.

Once the flow rate was properly adjusted it was possible to use
standards to optimize the heating rate. Figure 19 shows such a study
using a 2 µl of a 10 ppm PbCl₂ solution. Superimposed on the curve on
the right is the temperature of the furnace as recorded during that
cycle. These two curves in this diagram were drawn to coincide, but in
fact did not because the two recorder pens needed a separation space in
order for them to overlap. Serious problems with spurious signals were
encountered. These created difficulties in the interpretation of the
recorded signals.

It became evident from the lead chloride trace, as well as others,
that the approach of manually controlling the heating ramp would be
troublesome for the future identification of the different salts. The
numerous spurious absorption signals that were observed were ascribed to
Figure 17

Effect of Manually Controlling the PE Furnace Heating Rate. The best signal was obtained at fast heating rates. Peak trailing and differences were noted at lower heating rates.
PbCl$_2$, 1.5 µl 5 ppm

Figure 18

Purge Gas Flow Rate Using the Manually Controlled Heating Rate of the PE Furnace. Using a heating rate of $100^\circ$/10 sec. the optimum flow rate was 45 cc/min.
Heating Rate Study Using the Manual Procedure with the PE Furnace. The stepwise furnace temperature is depicted by the dotted line. The undesirable spurious signals that were more pronounced at slower heating rates are also depicted.
an increased atomization of the analyte each time the temperature was raised in steps. This effect was eliminated using the faster and more uniform heating rates which produced a smoother absorption signal.

The results obtained with some lead salts are depicted in figures 20 and 21. These show the signals observed for PbS and Pb$_3$O$_4$, respectively, and the marked incidence of the spurious signals. (2) Motorized heating rate: the two speeds of the kymograph provided two substantially different heating rates. One took about 20 minutes per revolution and the other about 26 1/2 minutes. Typically, the faster speed allowed heating from 100°C to 2000°C in 1 1/4 minutes, and the slower rate in 7 1/2 minutes. Figure 22 shows the signals obtained for two different concentrations of lead nitrate at the two heating rates. The signal temperature was not significantly affected by the sample size.

Using the faster heating rate produced a sharper, higher peak. The slower rate, similar to that used in the two stage AAS system, provided a sufficient temperature gradient so that differences in appearance temperatures for the various salts could be observed. The use of the slower rate also provided more accurate temperature measurements of the observed signals, since the actual furnace wall temperature lagged behind the electronic signal being recorded by about 5 seconds, when the faster heating rates were used.

For the studies on lead compounds the temperature program reached 2100°C, for cadmium 1800°C and for zinc 2000°C. It was not necessary to take the furnace to higher temperatures because by then all the samples had been swept away and the signal returned to baseline.

(g) Temperature assignment: because the recorder pens were
Lead Sulfide Absorption Trace Using the Manual Heating Rate Procedure with the PE System. Structure was observed at lower heating rates.
Figure 21

Observed Absorption Trace of the $\text{Pb}_3\text{O}_4$ Using the Manual Heating Rate Procedure with the PE System. The spurious signals were quite prominent and were undesirable.
Results from Samples of Two Concentration, at Two Heating Rates (motorized PE-HGA). Signals were sharper at fast heating rate but included structure at slow rate.
slightly offset, so that they would overlap, the temperature scale needed to be corrected accordingly. No other correction were included in the assignment of the temperatures.

(1) Furnace conditions: the dependence of the observed signal temperatures on the condition of the graphite tube is depicted in figure 23. A difference of about 200°C or more, was attributed to this effect for aged tubes relative to new ones.

![Figure 23](image)

**Figure 23**

Effect of the Graphite Tube Conditions on the Observed Signal Temperatures. At low furnace firing number the signals appear at temperatures closer to true values.

The carbon wall of the tube where the sample was placed thinned out with prolonged use. As a consequence, the same amount of electrical
power to heat the furnace to a particular temperature, the center portion of the graphite tube became hotter than normal. Since the recorder traced the uncorrected electrical temperature signal, provided by the furnace control unit, the assigned temperatures to the observed peaks were lower.

(2) Effect of sample size: in general, it was also observed that as the sample size that was analyzed with the PE system increased the appearance temperature of the signal decreased. It was thought that because of the highly dynamic conditions of the system that a sufficiently large amount of analyte was volatilized so as to be detected, when large samples were used. Conversely, small sample sizes did not volatilize enough analyte to be detected and thus their \( T_{\text{app}} \) was higher while the maximum of the signal did not significantly change in temperature. Figure 24 depicts the trend using lead chloride and iodide.

**2C.4. Two-Stage Atomizer.**

(a) **General Considerations:** the following were common to the first and second atomizers.

(1) **Signal processing system:** the PMT voltage used ranged between 500 and 650 volts. The signal from the PMT was fed through the junction box into the amplifier, which could only be operated with the chopper system engaged, in the phase-lock mode, and on the 100% \( T \) scale. To adjust for the optimum phase once the relative positions of the source, chopper and monochromator were fixed, the adjusting wheel (mentioned earlier under Light Source Modulation) was rotated until the
Effect of the Sample Size on the Observed Signal Temperatures
(a) For the lead chloride sample. (b) For the lead iodide sample. The appearance temperature decreased with increased sample concentrations.

Figure 24
largest signal was obtained. The amplifier was set to its $10^{-8}$ amp sensitivity scale for this study.

The recorder was only operated at the 100 mv scale and the chart speed varied depending on the heating rate used. For the most part since the preferred heating cycle lasted only about 5 minutes, a corresponding speed of 0.2 in/min. was used rather than 0.1 in/min.

(2) Atomizer gas flow rates: two streams of argon were used. The first went into the atomizer body and the second, through the analyzing tubes. Each was controlled separately.

All flow rate meters were calibrated by the soap bubble method, and with the respective gases flowing through them. The vacuum meter was calibrated from 0-280 cc/min drawing air.

The combined methane-argon flow rate going into the body of the atomizer ranged from 200 cc/min to more than a liter/min; the higher flow rates were used to purge the second atomizer, especially between samples.

The calibration of the argon flowing through the tube ranged up to ca. 140 cc/min. Flow rate studies showed the optimum to be near 110 cc/min.

During these studies two methods for metering the atomizer gases were used. The first utilized a diaphragm vacuum pump to draw the inert gases through the atomizer. The argon flowing through the analyzing sections was supplied excess at the injection port. A metered amount was drawn into the system while the rest prevented air entrainment. To insure proper argon flow rates going through the analyzing tubes the supply of excess argon was provided using a "T", at the gas entrance to
the atomizer body, and the injection port was closed after sample introduction.

The argon/methane mixture did not solve the problem of the formation of molybdenum blue inside the atomizer. This was attributed to the presence of oxygen, and resulted in the deterioration of the atomizer. It was very difficult to prevent air leaks through cracks in the atomizer and poor air seals.

Using a vacuum system exhausted all gases through the back of the atomization section. This diluted the atom population in the optical light path and reduced sensitivity.

The atomizer gases were subsequently directly introduced under positive pressure from the flowmeters. This second system eliminated the necessity of making the atomizer housing air tight.

The formation of molybdenum blue was still noticed on occasion. The oxygen leaks were traced to the seal at the top electrode. The second two-stage atomizer, though much better at eliminating the air leaks. A still tighter fitting teflon piece at the top electrode of this atomizer may improve the situation even further. However, such a piece was not available at that time.

One of the two most important parameters in the operation of this system affecting signal resolution was the flow rate of the argon going through the analyzing tubes. This entrained evolved gases from the heated sample into the atomization section. The other parameter was the heating rate, which is later discussed.

Lead chloride was used to observe the effect that the flow rate had on the absorption signal. The results obtained on two different occasions are shown in figures 25 and 26. It is important to point out
Figure 25

Effect of the Flow Rate of the Carrier Gas on the Lead Chloride Absorption Signal Using the Two-Stage Atomizer. At increased flow rate better resolution and fine structure were observed.
Further data on the effect of flow rate on the Absorption Signal Using the Two-Stage Atomizer. (Lead Chloride). This diagram primarily shows the important dependency of the low temperature peak on the flow rate.

Figure 26
that previous flow rate optimization studies had resulted in serious lack of reproducibility. Later studies showed that the distance between the analyzing sections was critical for reproducibility. The most important feature shown in these figures is the appearance of a low temperature signal with increased flow rates.

Typically, the molybdenum piece was allowed to cool down from white heat for about 20-30 minutes.

One can clearly observe the different shapes of the absorption signals as the flow rate was increased from figure 25. Higher flow rates than 130 cc/min could not be precisely measured with the rotometer used and were therefore not tried.

The results observed in figure 25 were at first surprising. The high linear flow rates involved implied short residence times in the atomization piece, where atomization and absorption took place. Figure 26 shows similar results obtained once the detection system had been further optimized. Dissimilarities observed between the results from these two figures were at first thought to be largely due to general irreproducibility problems of the system. Further studies later revealed that indeed there was a reproducibility factor involved, but also showed that these signals were due, in part, to sample section.

The most important result was the emergence of a sharp signal at low temperatures as the carrier gas flow rate was increased; high flow rates were subsequently used throughout the studies.

(3) Heating rate: The second important parameter for the optimal resolution of the observed signals was the heating rate. As explained in the Experimental section, heating times for the heating cycles were used to describe how fast the sample was heated.
Using a fixed flow rate the effect of changing the heating time was observed and the results are shown in figure 27. What was sought was a heating time which would allow reasonable resolution for speciation, trying to avoid possible overlap of the signals for the sample, thus minimizing signal broadening. It was found that the optimum heating time was about 5 1/2 minutes. Faster heating rates caused temperature measurement problems because of a time lag between the moment the power was applied and the actual heating of the component; the thermocouple used to monitor the vaporization section temperature also exhibited a time lag.

All of these sample introductions were done while the atomization section was at operating temperatures which heated the vaporization tube, by conduction to about 200-300°C.

(4) Temperature measurement and calibration: the temperature was measured with a chromel-alumel thermocouple placed just above the analyzing molybdenum tube (body-TC). The actual temperature at which volatilization occurred was difficult to measure. There existed a time delay between vaporization and the absorption signal. Proper calibration was required for good reproducibility.

(i) Optical pyrometer. Normally, the body-TC would heat up to 800-900°C, for equivalent vaporization temperatures of up to 2300-2400°C. A range of about 50-300°C, used with mercury compounds proved unsatisfactory. It was difficult to calibrate accurately above 1200°C even with the use of an optical pyrometer.

Figure 28 shows a different problem which was associated with changing the measuring scale of the pyrometer from high to extra high.
Effect of the Heating Rate on the Absorption Signal Observed with the Two-Stage Atomizer. (Lead Chloride). The 5 1/2 minute cycle was preferred because the signals were sharp and the heating time was practical.
Not knowing which temperature curve was the correct one made it necessary to calibrate the optical pyrometer. Several alternatives were possible, but not many were available especially when emissivities of the potential standards were taken into consideration. The main difficulty then was to obtain two, or more standard calibrated sources at relatively high temperatures.

![Graph showing temperature readings of the body thermocouple and the optical pyrometer.](image)

**Figure 28**

Temperature readings of the body thermocouple and the optical pyrometer. Not different readings on optical pyrometer using different scales. This error was eliminated by calibration.
The most convenient calibration approach was to use an electrical lamp. The 115 V, 40 W lamp operates at a temperature of 2750°K. This datum was insufficient, however, and an electrical power versus lamp temperature is the ideal information. As a result of correspondence with General Electric Co. the following equation was supplied by them enabling us to establish a temperature versus voltage plot:

\[ 2.7 \log(t_1/t_0) = \log(v_1/v_0), \]

where \( t_1 \) and \( t_0 \) are in °K, and \( v_1 \) and \( v_0 \) are voltages.\(^{105}\)

Figure 29 shows a plot of the temperatures, measured and corrected, which resulted from adjusting the instrument's scale to read the calculated 2000°K, instead of the observed 1800°K. No correction for the tungsten emissivities were included, amounting to about 25°C at 1800°C.

(ii) Thermocouple. The lower temperatures measured by the body-TC also needed to be calibrated. This was accomplished by correlating the measurements with those with another chromel-alumel thermocouple placed inside the vaporization tube. This other thermocouple was compared to the tube-protected thermocouple of the department glassblower's commercial annealing oven. Differences in measurements increased with temperature but were less than 3% at 600°C.

A new temperature calibration curve was needed each time the interior components were reassembled because the heating characteristics of the vaporization tube were not always the same for each assembly. The body-TC could only be repositioned over the metal tube where it got the
Calibration of the Optical Pyrometer with a Standard Source. The standard source was a 40 W (clear) electric bulb. Observed readings were connected to the calculated readings.
hottest (by visual inspection) with the second atomizer design. With the first atomizer, it was difficult to predetermine where the body-TC needed to be since once the assembly of the components was complete one was unable to observe the inside. (Using the second atomizer, it was noticed that after a few heating cycles the thermocouple needed to be cleaned from accumulated deposits.)

After obtaining several temperature measurements in both the low and higher ranges a working curve could then be constructed, (see figure 30) and subsequently used to assign temperatures to the observed absorption signals obtained with that particular assembly.

Proper injection of the sample was also extremely important in order to minimize temperature measurement uncertainties (discussed later).

![Example of a Calibrated Working Temperature Curve Showing thermocouple temperature and actual tube temperature.]

Figure 30
(5) **Distance between analyzing sections:** normally, this distance was about 1/4", or more, and when it was reduced to about 1/8" a significantly different absorption trace was observed, as depicted in figure 31b.

The results suggested that a partial condensation of the gases emanating from the heated sample was occurring within the carbon piece and between the molybdenum sections. The temperature of the carbon center electrode in this region was not as high as that of the vaporization tube. When this latter piece was not electrically heated, the former was usually hotter because of heat conduction from the hot atomization section. As the vaporization piece was gradually heated there was a temperature at which they were the same, namely, about 400°C. Following this the carbon piece lagged behind. (The maximum temperature that the carbon normally attained was about 600°-700°C.)

Also, the taper on the ends of the molybdenum sections, which were used in the latter portion of the studies, were thought to be conducive to decreasing any gas accumulation (partial "backpressure") between them.

(b) **Procedures specific to the First Atomizer.**

(1) **Interior components:** the molybdenum pieces were machined by the Chemistry and Physics Machine Shop to the dimensions specified in the Equipment section, one piece at a time, because variations were often introduced during the course of the study.

All the carbon pieces were machined by the author and were also described in the equipment section. Attention has to be drawn to the problems encountered when drilling these pieces. In general, all molybdenum pieces were 1/4" in diameter and it was extremely important
Figure 31
Results obtained by changing the distance between the Molybdenum Analyzing Section. Decreasing separation gave more intense signals.
that the holes drilled in the carbon pieces were exactly 1/4" in
diameter providing for tight metal-carbon connections the first time.
Serious difficulties were encountered stemming from problems with the
associated equipment that was used and the initial lack of experience in
their operation.

Examples of the above deficiencies include column mounting of the
laboratory's small lathe's head stock, as a drill press, and the need to
properly align it; there was also, a barely discernible wobble in the
lathe motor shaft which was later corrected; another source of drill bit
wobble was caused by worn drill chuck jaws; also, centering the carbon
pieces under the drill press could only be done by estimation, ...these
shortcomings, for the most part, were eventually surmounted.

Thermocouples were introduced in the first atomizer when it was
noticed that correlating temperature with the current being drawn to
heat the system was too uncertain and irreproducible. At first, the
thermocouple's temperature range was only 200-300°C on the TC gauge, and
corresponded to a maximum tube temperature of 2000°C. This body-TC was
eventually placed right next to the vaporization piece, thus providing
an adequate monitoring temperature range.

The power supplied to the atomization section was manually
controlled and set to a desired atomizing temperature. The power to the
vaporization section was also manually controlled rather than with the
motorized kymograph-belt system.

(2) Assembly of the system: the five interior components to
be assembled and fit rather precisely between the four brass electrodes.

The primary consideration was the atomization section and its
optical path which had to be aligned with the windows provided in the
atomizer housing and with the carbon center electrode. The last mechanical and electrical connection was made by joining the vaporization tube (already fitted into its carbon support and its brass electrode) with the center electrode, once the rest of the assembled pieces were properly fitted and aligned.

One of the major drawbacks with the first atomizer was that there were no viewing windows, so that once the system was closed not much could be seen inside. Another disadvantage was the difficulty in reaching the inside components which made the assembly of the system awkward.

(3) Testing and conditioning: once all the connections were joined, the only way of knowing if they were going to be durable was to actually heat the system. So after sufficient air purging, and having the cooling water flowing, the system could be turned on, and at the same time cleaned up for subsequent sample analyses.

A first glance indication that all was well, was the immediate flow of current when voltage was applied. As the system deteriorated a comparatively high voltage had to be applied before any current would flow (providing the heating). Under these latter circumstances, there was an uncontrollable and fairly sudden increase of temperature, with the thermocouple signal lagging far behind the actual tube temperature.

(4) Equilibrium temperature-depth profile: it was important for good reproducibility to place the samples in the hottest portion of the vaporization tube.

Each time the interior components of the atomizer were assembled it was necessary to determine the temperature-depth profile of the vaporization tube. This was accomplished by heating the tube to a
Figure 32

Temperature-Depth Profile on the Vaporization Section. The Atomizer was on in each case. Note a temperature maximum 0.5 cm from the center electrode.
convenient set of temperatures and at each setting, allowing sufficient
time for the temperature to reach equilibrium. The body-TC reading was
correlated with measurements obtained with another thermocouple
introduced into the tube, at various depths. A temperature profile
along the molybdenum tube at different power settings (temperatures) is
shown in figure 32. This profile indicated that the evolution of gases
from the sample would be observed at different temperatures when the
sample was not introduced at the same depth each time.

Temperatures above 1200°C were measured using the optical pyrometer
was used by looking down into the vaporization tube. No correction for
directional emmissivity was included.

Another consideration to the temperatures being measured was the
contribution from the atomization section, which was kept at operating
temperatures. The background temperature ranged unpredictably, from
about 150° to 300° C.

(5) Sample introduction: a long 4 in needle was used to
introduce the sample. A smearing problem occurred if the syringe was not
held, and withdrawn, steadily and concentrically because a slight
syringe movement caused a large needle tip travel. This problem was
alleviated to a large extent by using a injector support. Figure 33
shows its shape and the slot cut out on its underside.

Figure 33
Injector Support
Once the microliter volume of sample was hanging from the tip of the needle, the syringe was tilted so as to deposit the liquid onto the molybdenum piece at the predetermined depth. The syringe was then returned to its level position and then slowly and concentrically withdrawn.

(6) Heating cycle: the atomization section was always heated first to 1800-2100°C. The sample injection was marked on the recorder tracing right after the injection port was closed. Heating of the vaporization section was then started.

At first, the heating cycle was controlled by using the kymograph but soon after was changed to a manually adjusted mode. The procedure consisted in sufficiently increasing the power so as to produce a desired heating rate, for instance, a 50 degree per 90 or 60 sec. increase, as read from the body-TC gauge. This heating rate however, did not necessarily translate into a linear temperature ramp. Therefore, the total time it took for the maximum temperature to be reached was used as an indication of heating rate for the cycle.

A heating rate study indicated that a rate of about 50 body-TC degrees every about 20 to 35 seconds was the optimum (producing a sample analysis cycle time of about 10 or more minutes), as depicted by figure 27. These relatively fast heating rates of about 200-500°C/min. presented a problem in that there existed a time lag between the actual temperature and that observed at the body-TC. Every 50 degrees was marked on absorption trace with an event marker.

A heating cycle time of about 5 1/2 minutes was used throughout the studies because it was adequate for proper resolution of the signals. This rate amounted to a total average of about 360°C/min.
(c) Procedures specific to the Second Atomizer.

(1) Components: a higher degree of precision in machining the components was required than that acceptable for use in the first atomizer. The reason for this was that all four brass electrodes were designed and made so that they would invariably be positioned the same way each time the system was assembled. This was accomplished by threading these electrodes to fit a corresponding threaded ring on the atomizer housing. The top electrode which was spring loaded, slid through a teflon sleeve, accomplishing the same purpose as the threads on the other electrodes. The problems encountered in the preparation of these pieces were detailed in a previous section (Interior Components First Atomizer). Since further standardization of the assembling procedures were continuously sought, new details need to be described.

In the first place, the center hole which needed to be drilled in the carbon center electrode could now be marked with greater simplicity. The carbon piece was properly machined to fit the top and bottom electrodes and then was secured in its place. The front electrode was then introduced as far as possible into the atomizer and a 1/4" drill bit was slid through it until it extended beyond the brass electrode to mark the carbon piece.

Secondly, the hole in the carbon center electrode was usually drilled to 15/64" to ensure a tight fit with the 1/4" molybdenum pieces. With care it was possible to bore this hole to 1/4" to a depth of about 1/8" on each side. To drill the carbon piece to 1/4" on the second side it had to be turned over in the drill press and aligned again, but this proved to be difficult at times. In the carbon center pieces which connected to the latter tapered molybdenum sections, the
inside diameter was only 1/8". This provided a larger carbon to metal contact area and the details are shown in the last diagram of figure 4.

A second thermocouple was used in this atomizer to measure the temperature of the carbon center electrode. An opening for just such use in the housing had been anticipated and therefore no problems were encountered with this addition. Once the wires were fed through the hole, and positioned, the hole was sealed with silicone rubber sealant which also held the wires somewhat rigidly.

One improvement of the second atomizer was the addition of viewing windows. Two sets of doors were made one with windows 1 3/4" in diameter and the other set, with 2 1/4" windows. With each, 1/8" plate glass was used. Unfortunately these cracked on exposure to radiated heat. To alleviate this problem attenuators were made of aluminum foil by cutting slots out, thus exposing only about half of the glass. Additionally, rings of the appropriate diameter were cut out of a 1/64" thick polyethylene sheet and placed between the glass and the aluminum retainers.

(2) Assembly of the system: easy access to the interior made the task of assembling the components much easier, as did the properly aligned and threaded electrodes. Although a higher degree of precision was necessary in preparing the carbon pieces, any necessary adjustments were much simpler to perform since one could observe, and reach, all the pieces as they were joined together.

The sequence used was first to join the atomization section and its carbon support, and then press them together. As a unit they were subsequently pressed into the carbon center electrode which was already secured in its position. By turning the brass electrode enough pressure...
was applied and could be at the same time evenly distributed across the brass to carbon tapered joint. As this was done the carbon support was held steadily, to keep it from turning while the brass electrode was introduced further. The vaporization section was joined in like manner.

The introduction of the tapered connections created a new problem. As the system was heated the metal pieces expanded and softened to such an extent, that when any of the analyzing sections was cooled down, the other would automatically do so as well. This was due to the heat conduction affecting both sections. The tension keeping the conical surfaces together was relieved by reducing the temperature of the system. (Cooling contracted the metal pieces which had already slightly shrunk by softening, to accommodate the initial thermal expansion experienced by the system.) As a consequence of losing the electrical contact the atomizer had to be opened each time, mainly to hold the optical path on the molybdenum piece steady and keeping it from turning while the brass electrode was tightened again.

The setback suffered from the tapered pieces, could only be overcome by making the connections directly. The first attempt to do this consisted of holding the carbon supports with clamp-like collars around them. Figure 34 shows a diagram of the pieces involved. The attempt was not very successful because the collars were not sufficiently concentric so that once everything was tightened, heating created hot spots on the collar indicating that a large portion of the current was being conducted through these hot spots.
Figure 34

Exploded view of the electrodes. Note the collars which attached to the brass electrodes.

An alternative approach was to use 0.1 inch thick rings made to fit on the ends of the brass electrodes, fastened with several screws to the threaded holes already provided on the electrodes. Then the carbon supports were pressed into the ring and against the taper of the brass electrode, which as a result, held the two pieces fixed and provided additional electrical contact area. Only after completing the assembling sequence described previously were these contact rings fully fastened.

(3) Testing and conditioning: once the system was assembled the connections were tested. If on applying voltage the current immediately flowed then all was ready and the thermocouples would then be secured, the atomizer closed, and purged with argon.

Before introducing any sample the system was cleaned up by heating one section at a time, and waiting until the signal returned to baseline.
(4) **Equilibrium temperature-depth profile:** the same procedures used with the first atomizer were followed (refer to the corresponding section, b-(4)).

(5) **Sample introduction:** the main concern about introducing the sample was the depth at which it had to be placed. In this atomizer this distance was slightly larger than before. The inside diameter of the teflon injection piece was enlarged and drilled to the adequate depth, so that the syringe could be introduced deeply enough to reach the proper place where the sample had to go.

The introduction of the filter paper discs to the correct depth was achieved by using a length of glass tubing; also a nichrome wire served as the plunger to deliver the sample which had partially been fitted into the tube.

(6) **Heating cycle:** the procedure for heating the system up, measuring the heating rate as well as marking the absorption trace every 50 degrees, was the same as was used with the first atomizer. However, cooling the system down could not be controlled when using the tapered connections (refer to the above section (2)).

2C, 5. **Air sampling**

(a) **Sample collection:** the sampling site was the roof of the third floor administration offices.

The pump was left inside the hall so that no rain would fall on it, since sampling was going to be run uninterruptedly. The air was drawn at the rate of 3-5 L/min through the Gelman glass fiber filter paper which had been cut to fit the filter holder. The flow meter and the
Gelman holder were mounted a foot above the roof surface, and were covered to prevent any direct rain from falling on them.

(b) **Sample analysis:** it was found that 1/4" diameter discs were sufficient in size for analysis in the double stage atomizer. These were punched out from around the center of the filter because this latter portion appeared, by inspection to have more sample accumulated there. This was not surprising considering the design of the filter holder.

When the filter discs were introduced into the atomizer the injection port was opened and part of the argon flowing into the atomizer body came out through the analyzing tubes pushing the filter disc back out. Therefore, to successfully introduce the filter paper sample the argon/methane mixture was temporarily stopped until the injection port was closed up again.

2C.6. **Thermal analysis: TGA.**

TGA curves were used to identify intermediate and end products resulting from the thermal decomposition of the metal salts in an inert atmosphere. The primary reason for undertaking these analyses was due to the varying results reported in literature regarding the thermal degradation characteristics of several compounds. These disparities have been found to be a function of many parameters, a few of which include the gas atmospheres being used during the processes, the instrumentation's furnace designs; the source of the compounds also play an important role, depending on the absorbed or occluded components if the analytes were precipitated from solution; the initial amount of water contained within the sample was also found to affect the thermal
curves.

The TGA instrument was operated following normal procedures but could not be used for quantitatively measuring decomposition products. The problem was noticed when calcium oxalate monohydrate standards were analyzed and the baseline was not the same at the beginning and after the heating cycle.

In an attempt to find empirically, a baseline drift correction factor several other salts were used. No such factors could be found by using calcium carbonate, sodium oxalate and copper sulfate pentahydrate. Consequently, only qualitative information could be drawn from the curves, i.e. the temperatures at which the sample underwent processes involving weight loss, and therefore, parameters such as heating rate and purge gas flow rate were not stringently controlled.
3. RESULTS AND DISCUSSION.

All samples analyzed with the TGA were solid - following normal operating procedures with this technique. The maximum temperature obtained was 1000°C. Because of the high sensitivities of the AAS systems all the data obtained with the two-stage atomizer and the PE*403 unit utilized dilute liquid samples. This enabled samples to be examined within the concentration range of the instrument.

The major thrust of this work was to determine the capabilities of the two-stage atomizer as an analytical instrument, as well as its potential for metal speciation. The data that would be obtained with the PE system and the TGA were to be used to establish a correlation between the techniques.

The field of thermal analysis, as reported in the literature, exhibits a number of discrepancies and an attempt to settle some of these differences was not sought in this work. Consequently, the identification of each signal observed using the two-stage atomizer was therefore a difficult and time consuming task. In this study we did not attempt to verify the interpretations presented here since that would involve several years work.

3A. Standard Solutions.

3A.1 Lead Compounds.

(a) Acetate.

(1) TGA: the curve obtained for 14 mg of this compound showed a somewhat gradual decompositon occurring below 400°C. Figure 35 also shows the sample residue beginning to volatilize at 930°C.

(2) Two-stage atomizer: A sample of a 500 ppm solution was
Lead Acetate, 3 μl 500 ppm. (a) TGA; (b) Two-Stage Atomizer. Low temperature signals were obtained at 480, 700. The peak at 1500° corresponded to PbO (see figure 42).

Figure 35
used for the analysis. The absorption trace in figure 35 exhibited a prominent signal at 1500°C and also two smaller ones at 480°C and 700°C.

(3) Discussion: it was observed that the solid residue left in the TGA at 700°C was yellow and therefore was probably to be the monoxide. The absorption trace of the AAS system also coincided with that of the oxide.

(b) Carbonate.

(1) TGA: the TGA curve shown in figure 36 is that of a carbonate sample of 4 mg. Decomposition began at 290°C and showed to reach completion at 400°C. At 950°C volatilization of the residue was also observed to begin and at 1000°C the process was still taking place.

(2) PE graphite furnace: figure 36 also shows the absorption trace obtained with this instrument. The curve shows one signal which was observed at 860°C, at furnace firing number 108.

(3) Discussion: The TGA process left an orange-brown residue at 400°C and a yellow compound at about 700°C. Further volatilization of the sample above 900°C was similar to that observed with the acetate residue, and was later ascribed to the sublimation of the oxide.

The temperature observed for the carbonate (sample) using the PE system was lower than that anticipated (because of the decomposition of the carbonate to the oxide) This was due to the condition of the carbon furnace and its effect on signal temperatures (refer to the Procedures in the Experimental section).

(c) Chloride.

(1) TGA: a sample of about 2 mg began to volatilize at 550°C. Figure 37 shows how almost all the sample had essentially vaporized below 800°C.
Lead Carbonate, 3 μg Satd. solution. (a) TGA; (b) PE-HGA. The TGA curve indicated a low temperature decomposition at 400°C. No comparable peak was observed on the PE atomizer which cannot atomize at low temperatures.
Figure 37

Lead Chloride, (a) TGA; (b) PE-HGA; (c) Two-Stage Atomizer. Using the two-stage atomizer showed two prominent signals occurring at 310° and 1500°. Only one could be observed with the PE system because of its inability to atomize any species at low temperatures. The signal at 310° is believed to be due to the lead chloride. That at 1500° to the oxide.
(2) Two-stage atomizer: the temperature-absorption curve of 2 μl of 500 ppm of this compound is shown in figure 37. This curve shows two prominent signals occurring at 310°C and 1500°C. There also was a much smaller peak, like a shoulder, which was observed at about 700°C.

(3) PE graphite furnace: figure 37 also shows the results obtained by using 6 μl of 10 ppm. The peak is observed at 1120°C at a heating cycle number 31 with that graphite tube.

(4) Discussion: the visual inspection of the TGA's sample boat at the end of the heating cycle indicated that all the samples had volatilized. As a consequence, it was thought that the peak observed at 310°C using the two-stage atomizer was that of the lead is the chloride molecule. The high carrier gas flow rates used with this latter system is believed to have enhanced the volatility of the halide to some extent. In addition, the recorded temperature is most likely lower than the actual temperature, because of the fast heating rate used (refer to the temperature calibration of the system discussed in the Experimental section).

Also, work reported by Yasua and Kakiyama confirms this interpretation. They observed that the halides began volatilizing at temperatures ranging between 320-450°C, depending on the halide.

Using a TGA, Duval reported weight loss of the compound beginning at 528°C, and at 946°C he found both some chloride and oxide residues.

The signal observed at 1500°C with the two stage atomizer was higher than the corresponding peak using the PE graphite furnace. These two signals were probably due to the same species, such as the oxide. The reducing environment existing in the carbon furnace may account for the lower temperature observed in that system.
A third peak observed using the two-stage atomizer at about 700°C was thought to be due to a different species from those producing the other two signals. (The results presented in figure 31 indicated that the distance between the analyzing sections was very important.)

The lead chloride signal observed with the two-stage atomizer would not be detected with the PE system because it is below temperatures for atomization to take place. This important information confirmed that the two-stage atomizer will provide data not currently obtainable at such low concentrations by any other technique.

(d) Chromate.

1. TGA: the curve shown in figure 38 only shows a very gradual loss of weight up to 1000°C for a sample of 7.5 mg.

2. PE graphite furnace: figure 38 shows two peaks, at 800°C and almost 1100°C.

3. Discussion: this compound is said to dissociate at 757°C. It is thought that the signal on the PE at 800°C was due to the chromate, and the larger signal due, in part, to the oxide as a result of thermal decomposition. (The reducing environment present in the furnace affected the volatilization mechanism.)

(e) Iodide.

1. TGA: figure 39 shows how an 8 mg iodide sample lost weight beginning at about 450°C.

2. Two-stage atomizer: the absorption trace obtained for a sample of a saturated solution using this instrument also shown in figure 39. Much like the chloride, the iodide showed two prominent peaks: one at 330°C and the other at 1600°C. A shoulder on the latter signal is also observed to occur at about 1050°C.
Figure 38

Lead Chromate, (a) TGA; (b) PE-HGA. The absorption signal at 300° is believed to be due to the chromate, while that at 1080° to the oxide.
Figure 39
Lead Iodide, (a) TGA; (b) PE-HGA; (c) Two-Stage Atomizer. Note low temperature peak on two-stage atomization which is absent in the PE trace.
(3) PE graphite furnace: the result depicted in figure 39 shows the signal occurring at about 1170°C.

(4) Discussion: the TGA curve showed the sample to be almost all gone at about 600°C. Upon visual inspection of the sample boat after the completion of the heating cycle no sample residue was found. Thus, like the chloride it is thought that the signal observed at about 300°C with the two-stage atomizer was the halide molecule itself. The absorption observed for the lead iodide species using the two-stage atomizer is unique in that, at temperatures of 300°C no commercially available technique is capable of detecting the metal as such.

The analytical importance of these data is that sample decomposition involving volatilization of the metal can be identified and measured at low temperatures. This is not possible on the PE commercial instrument because atomization and hence atomic absorption does not take place at this low temperature. It should also be noted that the sensitivity is much lower than the TGA. This is a distinct analytical asset for some samples.

f) Molybdate.

(1) PE graphite furnace: figure 40 shows the results obtained with this compound; one signal was observed at about 1150°C.

(2) Discussion: the molybdate was expected to release MoO₃ upon heating, leaving a residue of oxide. Thus, the temperature observed for the signal was expected to coincide with that of the oxide. Figure 40 also shows the effect that increasing the sample size had on the appearance temperature of the peak.

(g) Nitrate.

(1) Two-stage atomizer: figure 41 shows that the most
Lead Molybdate Using the PE Furance. Note the decrease in the appearance temperatures as the sample size was increased. The peak coincided with that for the oxide (see figure 42).
Figure 41

Lead Nitrate, (a) Two-Stage Atomizer; (b) PE-HGA. Both absorption traces were found to coincide with those obtained for the oxide using the respective instruments. The signal at 950° with the PE furnace was slightly lower and due to the high furnace firing, number 78.
prominent peak occurred at 1500°C. Two smaller ones were obtained at 450°C and 700°C.

(2) PE graphite furnace: a peak was observed at 950°C.

(3) Discussion: The thermal degradation of this compound is described differently in literature. The trace was found to depend on the furnace atmosphere being used, heating rates, and so forth. Wendlandt found that initial decomposition of the salt heated in air occurred at 370°C, to an oxynitrate with its subsequent decomposition to elemental lead at 573°C. This latter step is not consistent with results obtained by other workers, who have postulated the decomposition to occur catalytically at 370°C to PbO, or via oxynitrates to finally produce PbO, and Pb₃O₄; Duval depicts the decomposition process taking place at 652°C to form the monoxide.

The result obtained with the PE system indicated that the oxide was being detected. Similarly, the absorption trace obtained with the two-stage atomizer also depicted the presence of the oxide. (Figure 41).

(h) Oxides.

(1) TGA: the trace observed in figure 42 shows weight losses from a sample of about 1 mg occurring at about 350°C beginning at 940°C, and still doing so at 1000°C, the maximum temperature reached by the instrument.

(2) Two-stage atomizer: figure 42 shows small peaks at 500° and 700°C and a large one occurring at 1500°C.

(3) PE graphite furnace: A signal was observed at 990°C (firing number 71) as shown in figure 42. The result of the red lead (Pb₃O₄) is shown in figure 43, and the signal for the smaller sample is observed at 1110°C (firing number 25).
Lead Oxide, (a) TGA; (b) Two-Stage Atomizer; (c) PE-HGA. The peak observed at 990° using the PE furnace was thought to be low because of graphite tube aging (firing number 71). The lower temperature relative to that observed at 1500° for the two-stage atomizer reflected the reducing capabilities of the graphite at those temperatures.
Pb$_2$O$_4$-red lead, Using the PE Furnace. Note the marked decrease in appearance temperature observed when the sample size was significantly increased. The system was overloaded with the large sample size.
(4) Discussion: since the oxides were insoluble in water appropriate amounts of the saturated solution was used to produce adequate absorption signals.

The monoxide was found to sublime above its melting point of 888°C in the absence of a reducing agent.\footnote{112} The volatilization observed at the higher temperatures on the TGA curve is ascribed to this process.

The monoxide was reduced to monomeric gas at 810°C using a carbon furnace (as a reducing agent) and at fast heating rates.\footnote{84} A higher temperature would be expected in a metallic furnace where no reduction would take place like in a graphite furnace. This was the case that was observed with the double stage atomizer (see figure 42).

The identity of the two small signals observed using the two-stage atomizer was uncertain. The large signal due to the oxide was characteristic of this compound and was obtained with the samples injected as solutions.

Red lead ultimately reduces to the monoxide. The literature reports several suggested mechanisms. These were found to depend on the conditions of the precipitation processes obtaining the salt, as well as its oxygen and water content, and instrumental parameters such as, furnace design and atmosphere, and so on. The signal observed on the PE system showed to be very similar to the monoxide.

(1) Sulfate.

(1) TGA: the TGA curve did not show any discernible weight loss below 1000°C using a sample of about 3 mg.

(2) Two-stage atomizer: As shown in figure 44, two signals were observed at 480°C and 700°C and a larger peak at 1450°C.

(3) PE graphite furnace: figure 44 also depicts an absorption
Lead Sulfate, (a) TGA; (b) Two-Stage Atomizer; (c) PE-HGA. The two-stage atomizer detected a signal at 680° which was characteristic of this compound. This peak was not detected with the PE furnace because of its inability to atomize species at those low temperatures.
signal at 1010°C.

(4) Discussion: the melting point of lead sulfate is reported to be 1170°C with decomposition taking place. Ostroff and Sanderson have reported the thermal decomposition occurring at 803°C using a DTA-TGA system. Other workers have observed it to occur in the range between 900 and 1250°C in a nitrogen atmosphere.

The two-stage atomizer showed a peak that was thought to be due to the oxide at 1450°C. It also exhibited a characteristic sharp signal at 700°C which could not be unequivocally identified, but suggested the presence of a different chemical form present. The presence of basic sulfates (or oxysulfates) resulting from the hydrated species introduced as solutions may explain this signal, which was not observed with the PE-HGA.

It is believed that the signal observed with the PE system at above 1010°C coincided with that of the oxide, once correcting for the heating cycle-temperature relationship.

(j) Sulfide.

(1) TGA: figure 45 shows the TGA curve of this compound. Weight loss began at 750°C, but the analysis could not be completed because of problems experienced with the instrument.

(2) PE graphite furnace: the results obtained using a saturated solution of this salt are shown in figure 45. A signal occurring at 1130°C was observed. Figure 46 shows the results that were obtained when using larger sample sizes, as well as the effect that was observed using different flow rates.

(3) Discussion: the melting point of this salt is 1114°C yet at lower temperatures than this it exhibited dissociation, depicted by
Figure 45

Lead Sulfide, (a) TGA; (b) PE-HGA
Effect of Sample Size: lead sulfide (a) 1 µl satd. solution; (b) 5 µl; (c) 2 µl suspension. The appearance of a signal at 920° with a concomitant increase in sample size suggested that this peak was due to the sulfide species.
the TGA as beginning at about 750°C.

The response observed with the PE*403 system exhibited a prominent peak at about 1100°C which was coincident with the monoxide. Also, as figure 46 depicts, a second signal emerged at about 900°C as the sample size was increased. This peak was tentatively thought to be due to the sulfide species since its intensity was small and directly affected by the concentration of the sample. The enhanced resolution observed at the higher purge gas flow rate can be explained, in part, by the atomic gases being swept away from the light path more quickly. This sweeping effect can also be observed by the decrease in signal intensities, for the 1 μl samples for example.

3A, 2. Cadmium Compounds.

(a) Acetate.

(1) TGA: the curve of this compound depicted in figure 47 shows weight losses occurring at 150°C and 300°C. A sample of about 6 mg of the dihydrate salt was used. (Melting points: 256°C)

(2) Two-stage atomizer: a sample of 0.5 μl 100 ppm cadmium, as the acetate, was used to produce the curve shown in figure 47. A prominent peak was observed at 600°C.

(3) PE graphite furnace: also shown in figure 47 is the absorption trace obtained from a 4 μl 0.5 ppm sample. The curve shows the cadmium appearing at 830°C.

(4) Discussion: the steps depicting weight losses in the TGA were not symmetric suggesting that the first was due to loss of the water of hydration, while the second was the decomposition to the
Cadmium Acetate, (a) TGA; (b) Two-Stage Atomizer; (c) PE-HGA. Note low temperatures peak in (b). Large peak may be the oxide.
oxide. After the heating cycle a grayish-brown residue was left indicating the presence of the oxide.

The two-stage atomizer exhibited one large peak which was later found to coincide with the oxide.

(b) **Chloride.**

(1) TGA: the TGA curve of the chloride showed a small weight loss of 8 mg sample occurring at 150°C. Another large one began at 600°C and the sample was almost all gone at 750°C.

(2) Two-stage atomizer: figure 48 shows two very large signals, one at 340°C and the other at 650°C.

(3) PE graphite furnace: the results using this system only showed one signal occurring at 850°C.

(4) Discussion: the TGA curves indicated two steps. The first step was attributed to the loss of the hydrated water molecules and the second to the volatilization of the compound. Visual inspection of the sample boat of the TGA after the heating cycle did not reveal any residue. Thus, total evaporation occurred before reaching its boiling point: bp 960°C, mp 568°C.

Tombeck proposed that sublimation occurred in nitrogen at red heat¹¹⁴, suggesting that volatilization of the cadmium chloride takes place in a similar fashion as with lead chloride.

Volatilization was observed with the two-stage atomizer at 340°C. Only one peak was observed at flow rates below 100 cc/min which indicated the high dependency of detecting the evolving gases upon the carrier gas flow rate at low temperatures.

The analysis conducted using the PE*403 system showed only one signal at 850°C. The lower temperature signal was not expected to be
The important feature shown in this figure is the detection of cadmium chloride at 340° using the two-stage atomizer. The PE carbon atomizer did not reveal this peak.
detected because of atomization efficiencies at these temperatures a
very low and therefore the evolved gases escape detection.

Low temperature volatilization has created losses when determining
this metal by conventional furnace AAS, producing some loss in
accuracy. It was also found that 0.5 ppm produced adequate absorption
signals, equivalent to 10^{-10} g absolute sensitivity. Sensitivities
normally obtained for carbon furnace AAS systems are two or three orders
of magnitude better. The two-stage atomizer will largely circumvent
this shortcoming, especially when analyzing solid samples.

(c) Iodide.

(1) Two-stage atomizer: figure 49 depicts the absorption
trace obtained with a sample of cadmium iodide. The thermal degradation
characteristics of this compound showed a signal at 340°C and 650°C.

(2) PE graphite furnace: figure 49 shows the resulting
absorption trace using this compound. The temperature of the signal was
observed to be 830°C.

(3) Discussion: the results obtained with the PE system for
the iodide closely resembled those from the chloride, when correcting
for the heating cycle number. Figure 49 only shows one peak.

The results obtained using the two stage atomizer depicted the
unique characteristic of this system, namely, its ability to detect
metal components that are volatilized at low temperatures. Thus, two
peaks were detected, one at 650°C and the other at 340°C which was not
observed with the PE+HGA.

(d) Nitrate.

(1) Two-stage atomizer: the trace shown in figure 50
exhibited only one peak at 700°C.
Cadmium Iodide, (a) Two-Stage Atomizer; (b) PE-HGA. The absorption peaks observed at 650° and 830° using the two-stage and the PE systems, respectively, coincided with the cadmium oxide signals. Only the two-stage atomizer detected a signal at 340° believed to be due to the iodide species.
Cadmium Nitrate, (a) Two-Stage Atomizer; (b) PE-HGA. The absorption trace of the two-stage atomizer indicated that the cadmium nitrate decomposed to the oxide at low temperatures. Both curves shown in the figure coincided with the respective traces using the oxide.
2 PE graphite furnace: the only signal observed using this furnace was observed at 760°C. (In ca. 810°C once corrected for furnace conditions.)

3 Discussion: the nitrate is decomposed to the oxide at temperatures of about 450°C. The signal observed with the two-stage atomizer was therefore, not unexpected and thought to coincide with that of the oxide. The corresponding peak observed with the PE system was observed at 810°C, corrected temperature, and was thought to be due to the oxide.

(e) Oxide.

(1) TGA: the TGA curve shown in figure 51 shows an weight loss occurring at 400°C using a 2.5 mg sample.

(2) Two-stage atomizer: the curve shown in figure 51 shows a signal occurring at 700°C using a 1 μg sample of a saturated solution.

(3) PE graphite furnace: a sample of 4 μl of a diluted saturated solution (400:1) was used to produce the absorption signal depicted in figure 51. The temperature was assigned to be 750°C, for a firing number of 201, therefore ca. 800°C once corrected (as shown).

(4) Discussion: the CRC Handbook of Chemistry and Physics lists the melting point of the cubic and amorphous forms of the oxide occurring at temperatures greater than 1500°C, and at the same time, reporting the amorphous form subliming at 900-1000°C. The results obtained with the TGA indicated weight loss at about 400°C, which was surprisingly low for sublimation to occur. Diverse results for the thermal behavior of the compound have been reported by other workers. It has been seen to dissociate below 600°C.114,115 Others have found it to volatilize in air at about 900-1000°C, with
Figure 51

Cadmium Oxide, (a) TGA; (b) Two-Stage Atomizer; (c) PE-HGA. Within experimental error the signals observed with each AAS system were thought to be about the same.
partial decomposition taking place.116 The latter authors also found that the oxide was reduced at 600°C in atmospheres of H₂, CO or in the presence of powdered carbon. Cotton and Wilkinson suggest that the compound sublimes at "very high temperatures".117 These various results emphasize the dependence of the data on experimental apparatus and procedures.

In the non reducing environment of the molybdenum atomizer (two-stage) the relatively low temperature observed for the oxide were thought to be due to the operating parameters of the atomizer, which significantly departed from equilibrium conditions. First the heating rate was in the order of 360°C/min and therefore not providing isothermal heating throughout the sample. Second, the atmosphere above the sample was not representative of liquid-gas equilibrium interface because of the large linear flows rates of the carrier gas. These were about 1 cm/sec.

The sensitivities obtained with the oxide sample, using the PE system were significant in that they were better than those observed for the soluble compounds. This was attributed, in part, to the lower volatility of the oxide (and the lower solubility) translating into smaller lower temperature losses.

(f) Sulfate.

(1) TGA: figure 52 shows only one weight loss step beginning at 200°C for a sample of about 10 mg.

(2) Two-stage atomizer: figure 52 also shows the absorption trace recorded with this instrument. The prominent peak was observed at 1000°C. A molecular background obtained using a deuterium lamp is also shown depicting the source of the small and broad signal observed at low
Cadmium Sulfate, (a) TGA; (b) Two-Stage Atomizer; (c) PE-HGA.
The results obtained using the PE furnace coincided with those using the oxide. The signal observed using the two-stage atomizer were at higher temperatures than those of the oxide. This suggested that under the operating conditions this salt did not significantly decompose to the oxide.
temperatures with the sulfate.

(3) PE graphite furnace: a 4 \( \mu l \) of 0.5 ppm standard is also shown in figure 52. The only signal was seen at 820°C, and analyzed at the furnace firing number 113.

(4) Discussion: the TGA curve showed a weight loss at about 250°C attributed to the loss of water (CdSO\(_4\)·7H\(_2\)O). The melting point of the compound is 1000°C, and visual inspection of the sample after the heating cycle revealed a white residue, which was the color of the initial substance.

Tombeck described the sulfate partially decomposing to oxysulfates at red heat, with the subsequent formation of the oxide at red-white heat,\(^{114}\) which would correspond to above 1000°C. He did not mention however, the furnace atmosphere that was used.

The PE system depicted the sulfate peak occurring at 820°C and coincided with the signal observed for the cadmium oxide. Without the reducing environment provided by the carbon, the signal was observed to be 1000°C using the molybdenum atomizer. This was higher than expected, thus suggesting that the sulfate did not show much decomposition under those operating conditions.

(g) Sulfide.

(1) TGA: A sample of 3.5 mg was used. The curve shown in figure 53 reveals that a weight loss occurred at about 800°C, under a stream of nitrogen.

(2) Two-stage atomizer: the signal that was observed using this system showed the maximum occurring at almost 700°C (see figure 53).

(3) PE graphite furnace: in figure 53 is also shown one of the results obtained with this instrument. The maximum of the signal is
Figure 53

Cadmium Sulfide, (a) TGA; (b) Two-Stage Atomizer; (c) PE-HGA. The absorption signals appeared at similar temperatures using both atomizers.
seen to occur at about 650°C. Figure 54 shows several temperature-absorption traces showing there probably was more than one signal that could be observed for the sulfide standard solution.

(4) Discussion: at the end of the TGA heating cycle no residue was noticed having thus all volatilized before reaching 900°C. Seed and Brasted reported that cadmium sulfide sublimed at 980°C in inert atmospheres. This is the same temperature that is found in standard handbooks for this salt.

A saturated solution was used as a sample to be analyzed in the AAS systems. The signal observed with the two-stage atomizer occurred at temperatures approaching 700°C; this was below its reported sublimation temperature, yet only 50°C below that observed with the TGA. This volatility was attributed in part to the dynamic conditions of the system, in particular the higher carrier gas flow rates. Also, the volatilization temperatures of the sulfide and oxide are reported to be very similar implying that if hydrated cadmium ions, i.e., cadmium oxide, were causing the signal it would appear at the same temperature. In other words, using the two-stage atomizer the sulfide and oxide signals were indistinguishable.

The results shown in figure 54 reveal the observation of possibly two species, in the diluted saturated solution sample. The higher temperature shoulder, or peak, was probably due to some oxide being present since the assigned temperatures were very similar with that of the oxide sample. In this case, the signal observed at 650°C was therefore probably due to the sulfide species, having had its volatility considerably affected by the carbon in the graphite furnace.

Once again it is interesting to note the improved sensitivities
obtained with this compound using the PE system, which were about an order of magnitude better than those obtained with the oxide. Paradoxically, the solubility product of this compound is reported to be \(1 \times 10^{-28}\), that is, having a very low solubility. This suggests that the low solubility and thermal stability enhanced the sensitivity and reduced losses of the metal at low temperatures.


The results obtained using the two-stage atomizer for the selected mercury compounds were of a preliminary nature since they were analyzed prior to the other metal compounds.

(a) Acetate.

(1) Two stage atomizer: this compound exhibited two sharp signals, as shown in figure 55, at temperatures of 70 and 130°. (These temperatures are not corrected because of calibration problems.)

(2) Discussion: the acetate is expected to decompose at low temperatures to the oxide. In air it does so at 180°C.

The serious problems encountered with the temperature calibration of the atomizer body-thermocouple inhibited proper assignment of temperatures to the absorption signals. Thus, it is thought that at about 70° (equivalent to about 200-300°C, starting temperatures) the signal was due to mercury being entrained with decomposition products. The other signal was most likely due to the volatilization of the residue in the range of 600-1000°C.

(b) Bromide.

(1) Two-stage atomizer: figure 56 shows the absorption trace that was observed and reveals a resolved but very small signal at 80°
Mercury (II) Acetate Using the Two-Stage Atomizer. The identity of the peak at higher temperatures is expected to be due to the oxide; the other, is uncertain. *Uncorrected temperatures. (See text).
Mercury (II) Bromide Using the Two-Stage Atomizer. The low temperature signal is believed to be due to the halide. The other peak to the oxide. *Uncorrected temperatures (See text).
(about 200-350°C) and a large one at about 110° (equivalent to 500-900°C).

(2) Discussion: the given temperatures above in parenthesis are estimated. At this time the instrument had not been properly evaluated and therefore at the lower temperatures the volatilization of the actual halide molecule was probably being detected. The prominent signal was thought to be due to oxide resulting from the dissolution process.

(c) Chlorides.

(1) Two-stage atomizer: in figure 57 are presented results obtained from the mercurous and mercuric forms of the halide. They showed similarities at the lower temperatures 80° and 95°; and they showed variations at 125° and 170°.

(2) Discussion: it was felt that these diagrams were rather approximative only since reproducibilities were not good. However, the low temperature signal observed for mercury(II) at 80° (200-350°C) was thought to be due to the volatization of the chloride itself. (The melting point is reported to be 276°C and its boiling point 302°C.)

The calomel is reported to sublime between 400-500°C which would indicate that one of the two signals recorded was probably due to this process. It is probably that at 95° we detected the volatilization of the halide molecule and at 125° the presence of oxide.

Later studies also revealed that a large part of the observed inconsistencies, and reproducibility problems were due to inappropriate sample introduction procedures (see the Experimental section for details).
Figure 57

Two-Stage Atomizer. The identities of the signals are uncertain. It is probable however, that the signals observed for the Hg₂Cl₂ were due to the halide and to the oxide, as the temperature increased. *Uncorrected temperatures (See text).

Figure 58

Two-Stage Atomizer. The observed peaks are thought to be due to the iodide and to the oxide species, at lower and higher temperatures, respectively.
(d) **Iodide.**

(1) Two stage atomizer: figure 58 shows the result obtained for this compound using this system. Two signals were observed: at 80° (200-350°C) and at 100° (400-800°C).

(2) Discussion: the thermal degradation characteristic was noticed to be very similar to that of the bromide; one could also look for and find resemblances with the chlorides as well.

The signal at 80° (200-350°C) was noticed to be very sharp. This suggested that volatilization was very sudden and suggested that although this phenomenon might be advantageous there was the possibility that the vaporization section was too hot at the sample introduction.

The chemical form of the peak observed at 100° (400-800°C) was not confirmed but was suspected to be the oxide, possibly brought about during the dissolution process. The oxide is reported to decompose at 500°C.

(e) **Sulfate.**

(1) Two stage atomizer: the trace presented in figure 59 shows considerable fine structure but was not thought to be significant. On the other hand two prominent signals could be discerned; one at about 75° (150-300) and the other at 160° (600-1200°C).

(2) Discussion: the sulfate is reported to decompose, and assumingly at low temperatures since none are given in handbooks. Thus, the signals observed at almost the same time as the introduction of the sample, was most probably due to the entrainment of metal with the evolved decomposition products.

The identity of the second signal at the higher temperatures was
Figure 59

Two-Stage Atomizer. The identity of the signals was not confirmed due to irreproducibility problems. The lower temperature peak occurred immediately after injection. *Uncorrected temperatures (See text).
not identified but was thought to be due to the oxide. Yet, the recorded temperature was higher than those observed with the other mercury samples. This could be attributed to several parameters including sample size, heating rate and others. It was then realized that procedural parameters needed to be carefully controlled before better results could be obtained. In addition, it was decided not to continue with mercury compounds because the initial temperatures of the vaporization tube were rather high for proper speciation of mercury to be carried out, and difficult to control. Thus, the advantage of detecting low temperature signals could not be advantageously used with mercury compounds at that stage.


(a) Acetate.

(1) PE graphite furnace: the absorption trace that was obtained for a 5 ppm solution is shown in figure 60, and exhibits only one signal, occurring at 1110°C.

(2) Discussion: Paulik and Paulik described the acetate to be a compound from which the oxide formed had a non stoichiometric composition, i.e., having a variable Zn to O ratio. They observed the decomposition occurring over a temperature range of about 800-1500°C. The only signal that was recorded using the PE system was later found to correspond to the absorption trace of the oxide.

(b) Chloride.

(1) TGA: the thermal decomposition obtained with this instrument is shown in figure 61 and reveals two weight loss steps. The first and small one occurred at 250°C and the second began at 450°C.
Zinc Acetate Using the Pe-HGA. This signal was observed to coincide with that of the oxide.
Figure 61

Zinc Chloride, (a) TGA; (b) PE-HGA. The signal observed at 1120°C coincided with that of the oxide. Peaks at lower temperatures were not detected because the furnace is unable to atomize any species of those temperatures. No peaks corresponded to the steps at 200 and 500 on the TGA.
showing a large loss of sample weight, meaning total volatilization at 650°C.

(2) PE graphite furnace: the signal that was observed at 1120°C for this compound is also shown in figure 61.

(3) Discussion: the zinc chloride is very deliquescent and forms oxychlorides in the presence of water. Thus, in loading the solid sample onto the TGA instrument some water was expected to have been absorbed by the salt. This accounts for the weight loss observed at low temperatures of the TGA curve. The large step ending at almost 700°C was attributed to the volatilization of the chloride compound. After completing the heating cycle no residue was seen in the sample boat.

For the analysis the PE system a 5 ppm chloride solution was used. Thus it was expected that oxychlorides were present, and this was reflected in the temperature of the signal that was observed. The chloride volatilization escaped detection because of the low atomization efficiencies of the furnace at the low temperatures, and because the non-atomized gases were also being automatically background corrected.

(c) Chromate:

(1) TGA: figure 62 shows the 0.7 mg sample losing weight in 2 steps in the temperature range of 350-400°C and 550-600°C.

(2) PE graphite furnace: a 1 μl sample of a 100:1 dilution of the saturated solution was used to produce the signal depicted in figure 57. The signal appeared at about 1020°C and its maximum occurred at 1120°C.

(3) Discussion: this salt is reported to be insoluble yet the signal observed with the PE system required a very dilute sample. This indicated that loss due to low temperature volatilization was
Zinc Chromate, (a) TGA; (b) PE-HGA. The TGA curve depicts the decomposition of the chromate to the oxide occurring at low temperatures. The signal observed with the PE furnace was later found to coincide with the oxide.
considerably reduced using this insoluble salt. This same effect was seen with the insoluble salts of cadmium, which is also a volatile element.

Using 1 μl of the saturated solution produced a signal that was much larger and broader than that shown in figure 62. Also, the T_app was reduced to about 980°C, which is what was observed to be the case when larger sample sizes were used using the PE system.

The decomposition of the chromate as shown by the TGA curve, left a residue at the end of the heating cycle, believed to be the oxide of zinc.

(d) Oxide.

(1) TGA: the TGA curve did not exhibit any discernible weight loss below 1000°C.

(2) PE graphite furnace: the signal observed with the oxide is shown in figure 63. It shows the peak occurring at 1110°C.

(3) Discussion: the melting point of this compound is 1975°C. It is therefore not surprising that no weight loss was observed below 1000°C using the TGA.

The reducing environment existing in the carbon furnace enabled the signal to be observed at below its melting point. The oxide has also been seen to dissociate within a rapidly heated carbon furnace at temperatures of about 870°C.84

(e) Sulfate.

(1) TGA: the TGA curve of this compound is shown in figure 64. Weight loss occurring at below 100°C, at 300° and beginning at 800°C were observed.

(2) PE graphite furnace: the absorption trace exhibited a
Zinc Oxide, (a) TGA; (b) PE-HGA. The TGA curve did not exhibit any weight loss below 1000°C. Reduction by the graphite in the PE furnace is thought to account for the observation of the signal at 1110°, considering that its melting point is 1975°C.
Zinc Sulfate, (a) TGA; (b) PE-HGA. The TGA curve showed decomposition to the oxide occurring at about 800°C. The absorption signal observed using the PE furnace coincided with that of the oxide.
single peak occurring at 1120°C, and is shown in figure 64.

(3) Discussion: the weight losses observed on the TGA curve below 350°C were attributed to the loss of water. The step observed between 800 and 950°C were due to the decomposition of the sulfate, leaving a residue in the sample boat. (Handbooks list the decomposition occurring at 600°C.)

In the carbon furnace AAS system such decomposition could not ordinarily be observed, especially if automatic background correction is used.

It was not possible to report any results obtained using the two-stage atomizer due to serious reproducibility problems encountered. These were caused by the high sensitivities obtained with the metal in AAS, and the presence of this metal, as an impurity, in the carbon pieces that were used as electrodes.

3B.-SOLID STANDARDS

For the analysis and speciation of solid (inorganic) samples the proper standards should also be solids. Since the atomic absorption system using the two-stage atomizer was so sensitive solid compounds could not be used. Small enough samples posed difficulties in handling.

An example is depicted in figure 65 which shows the absorption trace produced by a tiny lead chloride crystal. One limitation of using this approach was that the amount used for the analysis was too small to be weighed. Figure 65 also illustrates how the atomic line from the hollow cathode source was completely absorbed. In addition, the physically tiny crystal introduced into the atomizer appeared not to
The smallest possible lead chloride crystal produced total absorption of the lead resonance absorption line. Smaller samples could not be properly handled. The system was overloaded.
have been placed where the molybdenum tube was the hottest. This was observed by noticing the appearance temperatures of the signal which were shifted to the higher end of the scale.

As a result, standardization using solids was not pursued further and the development of an introduction system for solid standards became necessary for continued studies.

3C.-AIR PARTICULATE POLLUTANTS.

3C.1. Lead

A wide variety of lead compounds have reportedly been identified from collected particulates in air samples. In some cases, intricate instrumentation has been required in efforts to quantify results, especially when size distribution of the particulates was sought. Some of the lead compounds which have been identified include sulfates, ammonium lead sulfates, halides and oxyhalides, mixed halides, ammonium lead halides, sulfides, carbonates, and various oxides.

The results obtained using the two-stage atomizer are shown in figure 66. Three different samples were analyzed and are presented in the diagram, along with, their molecular backgrounds (at 280.2 mm) and a blank filter paper.

Filter No. 1 was used to scrub 25 3/4 m^3 of air. The collection period included rainfall which was expected to clean the air from some particulates. Filter No. 2 filtered almost 14 m^3 of air and the sample collection was stopped just before the first rainfall started within that sampling period. Filter No. 3 filtered 22.4 m^3 of air, during which rain did fall. This latter sample was collected over a weekend
The absorption traces of three different samples are shown in this figure. The top curve for each sample is the absorption observed at the lead resonance line. Below each of these is the molecular background obtained using the deuterium lamp. The signal observed at 1560°C in the first sample is believed to be due to oxides. The identity of the species producing the signals at 2330°C was uncertain. The traces indicate an oxide and two unidentified lead compounds.
Pb in Air Particulates

Figure 66
and the total suspended solids (TSP) amounted to 54 \( \mu \text{g/m}^3 \). Another sample accumulated the equivalent of 58 \( \mu \text{g/m}^3 \). Another one collected over a weekend when the vehicular traffic was expected to be lower than during the week had the equivalent of 68 \( \mu \text{g/m}^3 \) of TSP. Bullin and Moe found ca. 25 \( \mu \text{g/m}^3 \) of TSP measured at 75 ft from a road edge, and at an equivalent height of 40 ft.\textsuperscript{121}

The data presented in figure 66 of the air particulates (as solids) suggested that oxides were present in our samples and that oxyhalides or sulfates were also present. Quantification of these results could not be undertaken because of the difficulty involved with the use of solid standards. If there existed any organolead components in the collected samples they must have been present in very small amounts, if at all, because the molecular background absorption were essentially the same as the corresponding atomic signals at low temperatures. In addition, the procedure did not permit the careful evaluation of these compounds since little or no control of the lower temperatures was possible. Thus, at injections of about 200°C or above, immediate release of these volatile compounds would be eminent and subject to loss through the opened injection port.

The sample introduction procedure used for the filter paper samples still needed perfecting since they were rather large in physical size and therefore, not localized within the tube. As was mentioned earlier in the Experimental section, all samples needed to be precisely placed within the volatilization section.

Two different sample dispensers were used with the PE*403 system: a 10 \( \mu \text{l} \) pipet and a commercially available disposable one, each having
appropriate "plungers", as described in the Equipment section.

Figure 67 shows the qualitative and semiquantitative results obtained with filter No. 1. Superimposed on the larger signal is that produced by 3 μl of the saturated solution of PbO (which was shown in figure 42).

It was thought that the form of the lead was the oxide, as the assigned temperatures tended to indicate. To a first approximation, it was estimated that the lead particulate concentration in the air for that sample was about 0.1-1 μg/m³, which was within the range considered normal for ambient air. This result was arrived at from the solubility of PbO in water which produced 50 ng of lead, as the monoxide. Comparing the areas in absorbances, and the fraction of the filter paper sample used for analysis, one arrives at a figure of about 0.3 μg/m³ for the larger sample, i.e., using the disposable pipet, and about 0.6 μg/m³ using the 10 μl pipet.

3C.2. Cadmium.

The same procedure was used in the analysis for cadmium using the PE system as for the lead but no cadmium was detected, which was reassuring because of the degree of toxicity associated with cadmium.
Lead in Air Particulates Using the PE-HGA; (a) sample of 10 μl pipet; (b) of disposable pipet; (c) blank filter. Superimposed on the results seen in (b) is the absorption trace of the lead oxide, using the PE furnace. Extrapolation of these results in (a) and (b) indicated the presence of 0.1 - 1 μg/m³ of lead in the air.
4. GENERAL DISCUSSION.

4A. Advantages of the Two-Stage Atomizer.

The most prominent virtue of the AAS system is its ability to continuously monitor for metallic constituents of a sample that is gradually being heated. As a result, the chemical form of the volatile species can be identified at the low temperatures at which they evolve from the sample. This effect was clearly observed with the metal halides in particular. The lead sulfate also exhibited such a thermal degradation characteristic.

In contrast, other AAS systems which are commercially available do not have this capability because of their furnace design. The samples that are volatilized at low temperatures within these furnace do not atomize at those low temperatures, have escape detection.

Secondly, an important characteristic of this system is that relative to other thermal analysis techniques, such as the TGA for example, sensitivities are considerably better using the two-stage atomizer. This provides for a very desirable analytical attribute.

Thirdly, significant results can be achieved using this system. However, better control of some of the instrument's operational parameters would provide still better results and increased reproducibilities.

4B. Lead Compounds.

All the standards which were analyzed by AAS were solutions. In all cases the appearance of a signal which coincided with the oxide was observed, and in a few of these other peaks were also detected.

Among those lead compounds which only exhibited the same thermal degradation pattern as the oxide was the acetate, the carbonate,
molybdate and nitrate. Not unexpectedly these oxyanions of lead were also seen to decompose to the oxide by TGA.

The differences in the absorption traces that were observed with some compounds, such as the chloride for example, were found to be very dependent on carrier gas flow rate and heating rate, when the two-stage atomizer atomizer was used. The sulfate, iodide and chloride exhibited sharp signals below 1000°C distinguishing them from the oxide. Thus, only three of the compounds analyzed with this system, as solutions, stood apart from the rest. The major drawback to the lack of the speciation capabilities observed for the rest of the compounds lied in the fact that they were introduced as liquids — whether as standard concentrated solutions, or as saturated ones, for the insoluble salts. The hydration of the lead ions resulted in the formation of oxides of lead upon heating the samples.

Using the PE 403 system two insoluble salts of lead were analyzed which also showed the distinguishing features. These were the chromate and the sulfide. The thermal absorption curves of these two compounds also exhibited the oxide signal, also observed with the other lead salts, in addition to lower temperature peaks. For the chromate a signal occurred at 800°C and its intensity was seen to be highly dependent on the sample size that was used. The resolution of the peak was observed to increase with an increase of purge gas flow rate, but also with a partial loss of sensitivity.

The lead sulfide showed a similar response to that observed with the chromate using the PE graphite furnace, but the signal was at 900°C. Analyses of these two compounds were not performed with the two-stage atomizer. It is suspected that two signals would have been
obtained for each from standard saturated solution.

However, the characteristic signals observed for the lead chloride
and iodide using the molybdenum atomizer (at about 300°C), and that for
the sulfate (at 700°C) were not observed when using the graphite
furnace. It is believed that because the signals were automatically
background corrected using the latter system, the volatilized yet not
atomized analyte escaped detection. The evolved gases at these low
temperatures are not expected to be atomized in the graphite furnace.

4C. Cadmium Compounds.

The thermal degradation characteristics observed with the cadmium
compounds exhibited some similarities with those obtained with the lead
solutions. Namely, the chloride and halide showed two signals using the
two-stage atomizer. The first signals, at about 250°C, were attributed
to the cadmium halide species. These were not detected using the PE
system because of the low atomization efficiencies at those
temperatures, and also because the signals were automatically background
corrected.

The peaks observed at 650°C using the two-stage atomizer, for the
halides were attributed to the presence of oxides in the sample as a
result of the dissolution processes. These signals were the only ones
observed for the cadmium halides using the PE graphite furnace.

Some oxyanions of cadmium that were analyzed on both AAS systems
appeared to be indistinguishable from the results obtained with the
oxide. Among these were the acetate, the carbonate and the nitrate.
The sulfate exhibited a thermal-absorption curve similar to that of the
oxide using the PE system. However, in the non reducing conditions of
the two-stage atomizer the signal was observed at higher tempertures
than the oxide. It was observed at 1000°C which also is its melting point. The TGA curve did not exhibit any weight loss below 1000°C. It is thought therefore, that the volatilization of the sulfate from the molybdenum tube was highly dependent on its phase, i.e., as a liquid at the melting point. On the other hand, the presence of graphite seemed to have considerably affected this process considerably.

The results that were obtained with the cadmium sulfide were also unique from the other compounds in the following. The absorption trace obtained using the two-stage atomizer appeared to coincide with that of the oxide. At first this was not too surprising considering the low solubility of the salt and therefore the hydration of available cadmium ions. But, they are listed in the CRC Handbook of Chemistry and Physics to decompose and sublime at similar temperatures. The oxide at 900-1000°C and the sulfide subliming in nitrogen at 980°C (which is approximately what was observed from the TGA curve).

Using the PE system the sulfide exhibited apparent irreproducibility. Yet it is possible that the signal observed as a shoulder, or a not well resolved peak, at about 800°C was the oxide resulting from hydration of the ion. The other occurring at 650°C was then probably due to the sulfide species, the volatilization of which had been affected by the graphite. The T_{app} of this latter signal was far below those observed for the oxide.

An interesting observation was that of increased cadmium metal sensitivities when using the insoluble salts of the metal with the PE system. The saturated solutions of the carbonate, the oxides and the sulfide had to be diluted considerably otherwise the samples completely absorbed the analytical line of the slight source. This phenomenon was
thought to be due to the decreased volatility of the insoluble salts which therefore decreased the low temperature losses encountered in the graphite furnace. Calculating the absolute sensitivity of these compounds from the sample sizes and their solubility products showed that they were only about one order of magnitude away from those normally accepted for cadmium using graphite furnaces.

4D. Mercury Compounds.

The analyses of these compounds were performed prior to any shown and discussed in this dissertation. The halides that were used showed similarities among themselves but some reproducibility problems were encountered using the two-stage atomizer. The acetate and sulfate also showed encouraging results but again were beset with reproducibility shortcomings.

As a result of this work, however, important insight was gained in the operation and evaluation of this instrument. It was noticed that the sample injection technique was critical to good reproducibility because the molybdenum was not isothermal when it was heated. Thus, the samples needed to be placed always at the same place, and where the tube got the hottest. Also, it was important not to smear the sample within the metal tube.

Second, it was found that the flow of the carrier gas going through the metal analyzing sections was critical. Third, the heating rate was also found to profoundly affect the results. Fourth, it was realized how important it was to considerably improve the temperature calibration procedures of the body-thermocouple, so as to improve result accuracies. Sixth, it was found necessary to close the injection port
after sample introduction in order to insure that the sample went toward the atomization section and not be exhausted out the front of the atomizer.

Because the operating procedures involved having the atomization section at operating temperatures, little control of those of the vaporization tube were possible while the sample was introduced. As a result, the mercury standard solutions tended to boil and decompose as soon as they were injected. This seriously curtailed the possibilities of speciating mercury compounds and therefore no more efforts were expended toward this goal.

**4E. Zinc Compounds.**

The TGA curves of the solid standards of zinc compounds did show differences as would normally be expected. However, the same compounds introduced into the PE system as solutions did not. The recurring signal that was observed was that of the oxide, and was the case with the acetate, chloride, chromate and sulfate. The volatilization of any zinc chloride at low temperatures escaped detection because of the low atomization efficiencies in those circumstances.

The sensitivities for zinc were also not those usually accepted for standard zinc analyses, and were attributed in part to their loss at low temperatures, due to the high volatility that zinc has, much like cadmium.

Serious reproducibility problems were encountered using the two-stage atomizer because of the element being present in the carbon pieces used. As a result no data was available and no correlation could be made at that time.
4F. Air Particulates.

The results obtained by analyzing the filter samples were encouraging, in particular with regard to the qualitative aspect. Since these were solid samples the signal which were thought to be due to oxide for example, had to be present as such in the samples, or as a result of the thermal decomposition of some oxyanions, and not due to hydrated species as was encountered with the standard solutions. Although further development of an introduction system is needed for solid samples and standards the results obtained thus far provide an important basis for the continued development of this instrument and its applications.
5. **CONCLUSION.**

The most favorable attribute of the two-stage atomizer is its ability to distinguish the chemical form of metals present in a sample. Several standard solutions were analyzed in order to evaluate this capability and remarkable differences were observed. In particular, the lead halide compounds exhibited a low temperature signal that was characteristic of these salts, which are not normally detected using commercial atomic absorption systems. Another lead compound which exhibited a distinguishing feature was the lead sulfate. A signal was observed that was also characteristic of this compound when analyzed on the two-stage atomizer.

Other metal halides that were used also exhibited signals below 350°C. These signals could not be observed with the commercial PE AAS system because the volatilization occurred at temperatures that were too low for any atomization to take place. This was the case with some of the volatile compounds of lead, cadmium and zinc. As a result of this deficiency in the PE graphite furnace its sensitivities also suffer because these volatized portions escape detection. This shortcoming is not present in the two-stage atomizer.

Mercury compounds were also analyzed with the two-stage atomizer yet problems with reproducibility were encountered. These were the result of the initial difficulties experienced in controlling the operating parameters. In particular, control of the low (initial) temperatures proved to be difficult and therefore the results should only be considered as preliminary.
Attempts to alleviate these problems were not undertaken because mercury was only one of the many metals that were of interest, and the only one exhibiting such properties at the very low temperatures.

The sensitivities achieved with atomic absorption are several orders of magnitude better than those using TGA. Sample sizes that are required for the thermogravimetric analyses are in the order of milligrams and are considerably larger than those used with atomic absorption. Thus, the two-stage atomizer has a distinct analytical advantage over TGA in this respect, in addition to its speciation capabilities.

The results obtained with the two-stage atomizer clearly indicated the presence of oxides in the samples that were introduced as solutions. It is believed that this was the result of the hydration process taking place during the dissolution of the samples. Thus, when the species were heated the formation of oxides was inevitable.

It is essential in speciation that the chemical form of the metal not be disturbed prior to the analysis. Consequently, using standard solutions posed limitations and solid standards need to be used. However, because of the high sensitivity of atomic absorption these were difficult to use since small enough samples could not be properly injected. The need for an adequate system to handle such a small samples has to be developed.

Samples of air particulates were analyzed for lead using the two-stage atomizer and encouraging results were obtained. Namely, signals were observed at different temperatures suggesting the
presence of oxides and possibly some sulfate. However, more
definite conclusions could not be drawn at that time because some
operating parameters were difficult to control.

Other real solid samples will be analyzed with this system
with the ability of distinguishing the chemical forms of the
inorganic metallic constituents. Samples which will be of
interest include those from the field of metal corrosion, as well
as environmental pollution.
PART II

LASER INFRARED FLUORESCENCE AS A GC DETECTOR

1. INTRODUCTION.

Pioneering work performed in these laboratories in the late sixties was a major contributing factor in establishing the observation of laser induced infrared fluorescence. It was first observed in the wavelength region of 3 to 16 \( \mu m \) with ethane, propane and acetone, by Robinson et al.\(^1\) as early as 1968 (even though these did not directly absorb the laser radiation.) In later studies using the same laser-infrared system numerous other fluorescence spectra were reported, absorbing at 10.6 \( \mu m \).\(^2\) Several possible fluorescence mechanisms were suggested to account for the observed phenomena. At that time efforts were being made to measure air pollution concentrations remotely. There was a great potential advantage in remotely monitoring stack plumes and pollution levels over cities, and other remote areas.

Thermally excited infrared emission of \( \text{SO}_2 \) and \( \text{CO}_2 \) had been investigated by Low and Clancy.\(^3\) Their results were not quantitative however, because of the lack of information concerning the sample temperature. This was particularly elusive in billowing stack plumes which have widely varying temperatures. Since emission intensity depends on temperature and concentration, no useful quantitative data were derived.

Laser induced infrared fluorescence was proposed for the remote sensing of atmospheric pollutants. In this case fluorescence intensity depended on laser power - a measurable quantity. In 1974, Robinson and
Dake reported an evaluation of a hypothetical IR-laser remote sensing apparatus. They outlined the characteristics of such a system for detecting a concentration of 10 ppm of ethylene at a 100 km range, or 0.1 ppm at a range of 10 km.\textsuperscript{129}

These reported capabilities for a laser induced fluorescence system for the remote sensing were very encouraging. The concept of using IR-fluorescence as a gas chromatographic detector was also conceived at that time. Remote sensing took precedence however, because of the need for such a system to be developed, and made widely available for air pollution monitoring. Some published results\textsuperscript{130} were part of the author's Master's degree thesis was entitled, in part, "The Remote Sensing of Air Pollutants by IR Induced Fluorescence with a CO\textsubscript{2} Laser".\textsuperscript{131} Shortly after the completion of these pioneering studies the Chemistry Department was moved to a different facility which did not allow further work in this area. Hence, the time to develop the gc detector became propitious and efforts were then directed toward this task.

An infrared laser fluorescence detection system for gc has the potential capability of permitting the identification and characterization of gc eluants in situ. This coupling would provide a breakthrough in improving instrumentation for rapid separation and identification.

Chromatography has become a vital component in many laboratories for sample characterization by separating it into fractions. These fractions have been detected, and identified by many different approaches using combinations such as GC-MS, GC-UV and GC-IR. The use of lasers has not been widespread, and a review of that field follows.
IA. Non-IR Chromatography Laser Detectors.

Since this project is concerned with laser induced IR fluorescence we shall restrict our discussion to systems using lasers. Lasers are fast becoming most widely used sources of light - mostly because of their collimated beams, their monochromaticity as well as their strong irradiative power and temporal resolution we shall restrict our discussion using lasers.

In a recent example, Boutilier and co-workers\textsuperscript{132}, reported a system which could be used to detect non volatile fluorescein derivatives. In their on-line approach, the HPLC eluents were successively analyzed by UV-absorption and UV-fluorescence, as well as by coherent anti-Stokes Raman spectroscopy (CARS). Only in the latter analysis was a laser used. Their method was far from being refined at the time of publication, yet this approach holds great promise in the characterization of non volatile samples.

High sensitivities can be achieved with the use of laser induced UV-fluorescence, as was demonstrated by Diebold and Zare.\textsuperscript{16} They focused the ultraviolet-blue He/Cd laser beam onto an HPLC eluent drop without the use of a cell, and obtained a detection limit of 0.75 pg for aflatoxins. (These are toxins produced by a fungus or mold; aflatoxins are suspected to be carcinogenic). Another such example of extreme sensitivity was reported by Josefsson et al.\textsuperscript{133}, who used a krypton laser focused onto a free falling drop eluted from a conventional HPLC column, or a microcolumn. The laser induced fluorescence system was capable of measuring fluoranthene with a detection limit of 20 fg.
Detection limits which were several orders of magnitude higher than the above examples were obtained by other workers using a submicroliter flow-through cuvette which was based on the sheath-flow principle. At the cuvette, the flow rate was adjusted to 0.26 ml/min (having a back pressure of 14 atm) with a needle valve connected in parallel with the flow going into the cell inlet. Thus, having a laminar flow (Reynolds number of about 42) did not produce mixing of the sample flow with the sheath solvent, and detection limits of ca. 0.15 ng were obtained using porphyrins. Sepaniak and Yeung have used laser induced two-photon excitation fluorimetry with HPLC to increase the selectivity of their detection system. This selectivity was mostly a result of spectroscopic selection rules in the two photon absorption mechanism. The disadvantage suffered in sensitivity by the gain in selectivity was partially recovered when considering that this type of fluorescence will not occur near the Rayleigh frequencies, and therefore neither Rayleigh nor Raman scattering interfered. A good review article concerning laser fluorimetry in liquid chromatography has also recently been published by the same authors.

A still different approach was the one used by Klimcak and Wessel to measured polyaromatic hydrocarbons (PAH) by resonance enhanced 2-photon photoionization. They used a laser to induce ionization and measured the electrons ejected by the PAH's with a proportional counter detector, with a detection limit of about 10 pg. Zare also reported the detection of aflatoxins at sub-nanogram levels, by using laser induced fluorescence coupled with TLC. Other applications of lasers are continuously being sought and emerging, providing a rather broad horizon of alternatives.
IB. Chromatography Detectors using IR.

Infrared spectroscopy has been limited for a long time by the relative lack of sensitivity. However, with the advent of IR lasers this technique has flourished considerably. Improvement is also due to more sensitive IR detectors which are now available, namely, the triglycine sulfate detector (TGS) among the pyroelectric detectors, and the cooled infrared detectors, examples of which include the photoconductive and photovoltaic mercury cadmium telluride detectors (MCT). But with more powerful sources care must be taken in the standard absorption techniques to prevent possible damage of these more sensitive detectors.

When coupled to chromatography, infrared has been used in its various modes. Some examples include that of Alt and Szekely in which they used TLC-IR absorption[^138]. In their system, samples of dyes and their intermediates were separated using a TLC plate and subsequently analyzed the separated fractions by IR absorption using the KBr pellet technique. Liquid chromatography has also been used in conjunction with IR detection systems as reported by Vidrine and Mattson[^8]. In their preliminary work they used gel permeation to look at 0.5 μg levels of paraffin oil in samples. Their detection system consisted of a Fourier transform infrared instrument (FTIR) to measure the paraffin oil in real-time.

Diffuse reflectance FTIR has been used with HPLC by Kuehl and Griffiths[^139]. They were able to measure sub-microgram levels of azobenzene isomers with their method which involved a somewhat elaborate, computer controlled interface between the sample separation
and analysis. The eluents in this system were collected in KCl filled cups fitted on a disc, from which the solvent was subsequently evaporated and followed by the IR measurements. Other HPLC-FTIR applications are also found in literature but have not been as frequently reported as other systems which have coupled gc to infrared.

The use of interferometry with IR was first proposed in 1966 by Low and has grown to play a very important part in the instrumentation of numerous laboratories and providing considerable improvements in sensitivity levels. The applications of FTIR-GC has mushroomed in the last decade.

In a general overview article Coffey describes the system and methodology. An MCT detector is most often used because of its available sensitivity which is very advantageous in FTIR systems since they operate in the absorption mode, with conventional sources. The interfacing of FTIR with the GC is somewhat critical because the connections must be such that eluant resolution is not lost. The light pipe (or absorption cell) must also be as long as possible to increase sensitivity, since absorption is proportional to the path length. Consequently, most light paths are small in diameter, having varying lengths. One difficulty that a small cell presents is the ability to focus the infrared beam onto the entrance window; these themselves have to be unaffected by the chemicals being used as well as the surrounding atmosphere (humidity in particular). Many of these shortcomings have been satisfactorily resolved in the commercially available instruments. Another very good review article by Erickson concerning GC-FTIR was published in 1979.

Fourier transform-IR has been successfully applied to samples
eluting from capillary GC columns.\textsuperscript{5,142} The development of double beam FTIR has also been fruitful in achieving the reduction of background noise, as well as increasing sensitivity.\textsuperscript{142,143} Another FTIR application is that reported by Wilkins and co-worker, in which they were successful in their initial attempts at complementing GC-FTIR information with an on-line high resolution MS.\textsuperscript{23}

In all the previously mentioned approaches using IR as detection systems, infrared lasers were not included and these have in fact not been coupled with gc to any large extent. The most important advantages as IR sources include their power density, and their wavelength tunability, which would then exempt the detection systems from having to use interferometers, as well as any energy dispersing devices, such as monochromators. Infrared laser tunability has however, also been an impairment to the successful wide application of IR-lasers as detectors, since their spectral range are in fact limited. It should be mentioned that remarkable improvements have been achieved in the last few years with free electron lasers, providing a broad wavelength range of tunability, as well as diode lasers, for example lead salts, which are reportedly tunable in the IR region between 3 and 30 μm.

One example using an IR laser-GC system has been reported by Lin et al.\textsuperscript{144}, in which they used a heterodyne detection system having a tunable CO\textsubscript{2} laser to overlap an absorption band of the eluting solute. With this procedure they achieved detection limits of 1 pg for SF\textsubscript{6}. Another example in which a CO\textsubscript{2} laser was successfully used is presented by Kreuzer\textsuperscript{145} in which the GC detection system is based on laser optoacoustic spectroscopy, obtaining pg levels for detection limits of ethylene and 2-pentanone. One drawback to this latter approach was the
lack of selectivity.

IC. Proposed Infrared Fluorescence Detection.

Laser induced infrared fluorescence has been studied for several years in these laboratories in an effort to develop a system for remote sensing, and one which could serve as a gc detector. The results obtained during these early stages include recording the induced fluorescence from dozens of compound and looking at, interference studies, as well as lifetime measurements of some excited molecules. 146-149

This phenomenon of laser fluorescence allowed to observe emission at shorter wavelengths than the source, as well as at longer ones. Therefore, by using a powerful CO₂ laser, in conjunction with a sensitive infrared detector, infrared fluorescence of gc elutants was going to be sought and measured, and since this method was non destructive other complementary on-line detection system could also conceivably be introduced.

The purpose of the work was to develop an interface between a GC and a laser induced IR-fluorescence detection system. The optics of a previously modified IR-spectrophotometer were used to obtain infrared fluorescence spectra of the eluted fractions. Alternatively, the wavelength of a particular functional group could be monitored, since fast scanning was not possible with the available instrumentation. Still another approach used wide band filters to select a broader energy window of the emitted radiation.

A time delay measurement of the signal with respect to the source modulation could also be used (i.e., phase shifting) providing a method
for distinguishing between source radiation scatter and fluorescence. Phase shifting with the signal amplification system would not provide a substitute for an energy dispersive system, and therefore, could not provide a method of qualitatively identifying compounds.

A fluorescence cell had to be designed to meet several requirements. First, it had to be infrared transparent and unaffected by heating (if it absorbed laser radiation). Second it had to be inert to the ambient atmosphere and chemicals that were going to be used. Thirdly, the cell had to provide a fluorescence window large enough to place a detector next to it, or alternatively, providing a large solid angle so that a gathering mirror could be used to collect and focus the radiation onto the detector. Fourth, the cell had to be compatible with gc parameters such as flow rate and sample size. Fifth this cell also had to preserve peak resolution.
2.- EXPERIMENTAL

2A.- EQUIPMENT.

2A.1 - Lasers.

(a) Perkin Elmer Model 6200 (Quasi-continuous CO\textsubscript{2}). Operating power of 10-28 watts/cm\textsuperscript{2}. Principal lasing line of 10.6 \textmu m.

(b) Metrological Instruments Model 210 He-Ne laser, 0.5 mW. (Used to align the system.)

2A.2 - Chopper.


2A.3 - Gas Cells.

(a) A large gas cell (with its approximate dimensions), depicted in figure 68, was initially used in the studies. The laser beam passed through the IRTRAN window, entered the gas cell, and was reflected by the mirror. The output beam was collected by the detector above the cell.

Figure 68

Large Gas Cell with IRTRAN Windows. The gases were introduced into the optical path of the laser beam. Infrared fluorescence was collected by the mirror and focused on a detector placed above the cell.
beam windows and the detection one, had IRTRAN II (ZnS) windows which transmitted the IR radiation of interest. The cell also included a short focal length, front surface aluminized concave mirror, 2 inches in diameter (and 2 inches focal length).

(b) A smaller cube cell constructed from IRTRAN II material is shown in figure 69. All components were joined using Torr Seal (low vapor pressure resin) obtainable from Varian Assoc., Vacuum Division.

![Figure 69](image)

**Figure 69**

Cubic IRTRAN Cell. The Copper wire was used as support.

2A.4 - Gas Chromatographs.

Two chromatographs were used: the first was an Aerograph Autoprep, model A-700 having an 8 foot, $\frac{1}{4}$ inch, 15% SE-30 (50/80 mesh) column; the detector was a thermal conductivity system. The second was a Beckman GC-II with the same column previously mentioned, also having a thermal conductivity detector.

2A.5. - Infrared Detectors.

(a) Barnes Engineering model 662 triglycine sulfate (TGS) pyroelectric detector with an F.E.T. amplifier. Area: 0.04 cm², detectivity: $8.1 \times 10^8$.

(b) Charles M. Reeder and Co. thermocouple detector: RBK-77S
CsI. Figure 70 shows a diagram of the shape of the detector as well as the housing that was built for it to keep ambient moisture from deteriorating the CsI lens.

![Diagram of CsI detector and housing](image-url)

**Figure 70**

Thermocouple with CsI Lens and Housing to Protect It.

(c) Thermocouple/IR-10 a Beckmann IR-10 infrared spectrophotometer was also used in the latter part of the studies. The detector which was found in it (a Charles M. Reeder RBK-55S, No. 14620 with a CsI lens) was soon changed to a PE No. 16676, KBr lens thermocouple (which had been used before in another instrument), because it was thought that the former was not operating properly.

2A.6 - Laser Power Meter.

Coherent radiation model 201 power monitor. Maximum capable power of 100 watts.

2A.7 - Signal Processing and Recording Equipment.

(a) GC system. The signals produced by the Aerograph GC system was fed directly to a Barber-Colman 10 mv potentiometric recorder, model No. 8000-2600. Alternatively, another Barber-Colman Wheelco recorder (same model) was used which was part of a Barber-Colman
model 20 Gas Liquid Chromatographic Ionization Detection System. (This recorder was utilized by-passing its electrometer amplifier.) The Beckman GC II signals required the use of an adjustable potentiometer between the latter recorder and itself.

(b) Laser-infrared system.

(1) The laser power could be followed and recorded if the signal from the power-monitor was fed into a Texas Instrument dual overlapping pen servo/riter II recorder, which only had a 1 mv span. As a consequence of the small recorder span a Helipot Corp. precision potentiometer, model T-10-A, was used to tap the appropriate signal amplitude from the laser power monitor.

(2) All signals produced by the infrared detectors were fed to a PAR model 124 lock-in amplifier, having a PAR model 116 differential preamplifier. Once exception was the use of an amplifier built by the Chemistry Electronics Shop. For a time this was used to receive the signals from the TGS detector. This system was in operation when electronic noise in the laboratories was excessive, causing the phase sensitive detection system to unlock from the reference (laser modulation frequency), rendering the PAR system unusable. A diagram of this substitute amplifier is shown in figure 71. Several recorders were used with these amplifiers but for most of the work the dual pen servo/riter II, mentioned above, was utilized. (As before, an appropriate electrical system needed to be used to match signal input and the recorder's 1 mv span).
As the studies proceeded and the cells were changed, the gas system also changed considerably. Figure 72 depicts the initial set up which was used, in which the exhaust of the gc was connected to the larger cell with over a foot of tygon tubing. Soon after, the use of a diaphragm pump (Dyna-Vac Pump, model 4K by Cole-Palmer Instrument Co.) was thought to be necessary so as to draw the gc eluting fractions once the had been exposed to the CO$_2$ laser beam (also shown in figure 72).
With the use of the IRTRAN II cubic cell the gas system was modified further so as to accommodate the use of a N₂/ethylene gas stream, which was going to be used for the alignment of the optical system. Figure 73a depicts this set up, and part b shows the further modifications needed, because a more adequate stop-flow system was necessary to optimize the detection system. (This was particularly the case when using the IR-10 infrared spectrophotometer.) These two latter gas systems included a provision to bring them to atmospheric pressure with nitrogen. Once they did reach atmospheric pressure nitrogen would bubble under water in the bubbler chamber. Once nitrogen was seen to bubble the three way valve under the IRTRAN cell was closed to maintain the ethylene sample static and unperturbed. (Monitoring the absorption of the laser beam showed that the system was quite stable until the ethylene was evacuated and purged.)
Figure 73

Gas System Used with the IRTRAN Cubic Cell (a) Flowing system; (b) Static system. These systems provided a source of fluorescence in order to properly align the detection system.
2A.9 - Optical Arrangements.

(a) **Larger cell.**

The focal length of focusing mirror of the cell was such that fluorescence emanating from within the laser beam would be focused somewhat above the detection window of the gas cell. Therefore, the detector could not rest on the window itself but was fixed above the cell. A drawback which resulted from this was that the solid angle described by the mirror was truncated at the detection window. This system is depicted in figure 72. Optimization with scattered radiation from a wire, which was introduced within the cell, was very difficult because the position of the wire was extremely critical. This alignment problem accounted for one of the major drawbacks of using this optical system.

(b) **Cubic IRTRAN cell.**

Figure 74 depicts the optical arrangements used with this smaller cell. Optimization of the alignment was attempted with and without the use of a 2 1/2" diam concave mirror (having the appropriate focal length). This was again repeated when the IR-10 spectrophotometer was used. This optimization approach was undertaken using a scatter site as well as with the laser emission from within the cell. (The scatter site which was used was in the form of a length of a wire ranging in diameter between 0.16 mm and 1.0 mm.)

The different diagrams in figure 74 are quite explicit and have the mirror positions highlighted to underline differences. Only in part (a) was the TGS detector used, because soon after its sensitivity dropped
FIGURE 74

(a) A mirror is used to gather radiation emitted from the cube cell and focused back through the sample cell to the detector.

(b) A thermocouple detector is used and placed next to the cube cell. The gathering mirror is used to refocus the transmitted laser beam back into the cube cell. This considerably increased the available radiant laser power.

(c) The gathering mirror is used to focus the collected radiation onto the detector in an offset position. This avoided the radiation being focused from traversing the cube cell, and eliminated any radiation being blocked by the edges of the cell. (Compare with figure (a)).

(d) A commercial (modified) instrument fitted with a thermocouple is depicted. This instrument had previously been used to obtain the IR-fluorescence spectra of numerous organic compounds. The arrangement of the entrance slits and detector did not allow to place the gathering mirror in any other position other than that depicted.
Figure 74

Optical Systems Used with the IRTRAN Cube Cell. (a) Using the TGS detector; (b) and (c) show different arrangements used with a thermocouple detector. (d) System using the IR-10 instrument as a detector (it also had a thermocouple detector).
off. (Also, the power meter not only served to continuously monitor
the laser power but also provided a sink for the laser beam being
transmitted through the cell.)

2B. - GASES.

The gases used for the gc were nitrogen and helium, with the latter
being mostly used for the optimization of the gc peak resolution when a
mixture was injected. They were obtained from Lincoln Big Three Co.,
and Airco Inc., respectively.

Other gases included:

(1) Carbon Dioxide - C.P. - Matheson Co.
(2) Ethylene, C.P. - Matheson Co.
(3) Propane, C.P. - Matheson Co.
(4) Propylene, C.P. - Matheson Co.

Ethylene was the gas of preference when seeking infrared
fluorescence because it was the strongest absorber, and emitter, among
those which had been analyzed in these laboratories; propylene was the
second choice. They were also used because at room temperature they
were gases making them easy to handle, as well as simplifying the
preparation of known volume concentrations (in a nitrogen atmosphere).

Nitrogen was cleaned with activated charcoal and dried with silica
gel, in particular toward the end of the study because of the
difficulties encountered in observing fluorescence.
3. RESULTS AND DISCUSSION.

The results will be presented according to which gas cell-detector combination was used: two cells were utilized, and fluorescence was sought with essentially three detectors, providing four systems altogether.

3,A. Large cell - TGS detector.

The advantage which was thought would be gained by using the larger cell, since it had a focusing mirror, did not materialize. The focal length of the mirror was such that the detector had to be placed above, and removed from the cell. Another problem was the aligning these two components. A metal wire was introduced into the cell to provide a scatter site within the laser beam, in the region from where the fluorescence was going to be collected and focused by the mirror. This did not prove to be easy. First, the optimization of the wire-mirror-detector alignment system only applied to the small volume within the cell where the laser beam reflected from the wire. Secondly, since scattering was highly directional, the wire did not necessarily provide a substitute for the fluorescence source, which is isotropic. And thirdly, the size of the TGS detection element was small which severely limited the amount of radiation falling upon it.

Consequently, use of the scatter site was discontinued and the gc effluent was channeled through an 1/8" id teflon tubing into the gas cell. The tip of the tubing was placed on the edge of the laser beam so that no scatter would occur and also to avoid the tubing from being thermally decomposed. As a result, the detector needed to be aligned
with the small volume of the laser-beam just beyond the teflon tubing (This is depicted in figure 56).

If the detection system was not perfectly aligned then the appearance of the elutant would be missed and the only time that fluorescence was observed was when the eluted sample peak filled the gas cell. However, this also presented a severe sensitivity limitation because of the dilution effect that the eluant suffered within the cell. In addition, if the gc components lingered within the cell, rather than promptly being exhausted, interference problems were encountered. A vacuum was applied to alleviate this problem. However, fluorescence was not be observed using this system. It was thought that since the size of the gas cell was too large, a smaller one was needed; the realignment of the system still had to be undertaken and the length of the tubing from the gc to the gas cell also needed to be shortened considerably.

3,B. Cube cell - TGS detector.

One of the predominant considerations in designing the cube IRTRAN cell was to reduce the size of the cell to preserve gc peak resolution. However, it was necessary that it remained large enough to accommodate the laser beam cross section entering the cell. It was decided that the faces of the cube would be one cm² each. This was smaller than the laser beam's one in ² diameter. As a result (as depicted in figures 72 and 74) an iris was placed in front of the cell. Otherwise the laser beam irradiated the edges of the cube, which would subsequently deteriorate the adhesive holding the cell together by the excess laser
heat. Decomposition products of the adhesive would also have presented additional problems.

Figure 74a shows how the system was set up diagramatically. It also shows how it made use of an appropriate mirror to collect and focus the radiation being emitted from the cell in the opposite direction from that going straight to the detector. (This arrangement had also been tried without the use of the mirror by placing the detector up against the cell window.)

As the laser power transmitted through the cell was being monitored, one could observe slight fluctuations as the eluting compounds from the gc passed through the cell. (The gc thermal conductivity detector signals provided a time reference for the observation of the peaks at the gas cell.) Since the laser "absorption peaks" were so small one could not be too sure that fluorescence was occurring at that precise moment in time because the laser itself exhibited inherent instability, creating background laser power fluctuations.

The only emitted signals from the cell which could be observed were those from a scatter site introduced into the system for preliminary alignment purposes. Even these were later no longer seen and the problem was finally traced to the detector which, even after repoling, showed no response to signals provided under test conditions. Thermocouple detectors were subsequently used with no sensitivity reservations since most of the fluorescence spectra obtained in previous work by others in this laboratory, were recorded using an IR-10 infrared spectrophotometer fitted with such a detector.
3,C. **Cube cell-thermocouple.**

The optical arrangement shown in figures 74b and c were used with the thermocouple detector and the gas system had a very short connection between the GC and the cell. In the first attempts, no fluorescence could be observed and the signals that were seen resulted from scatter off a wire in the cell during alignment procedures. Several injections of about 2-4 cc of ethylene, going through the GC system, gave no signals.

3C.1 **Flowing ethylene fluorescence source.**

A gas system was devised in which a constant mixture of a nitrogen-ethylene stream flowed through the cell, so that alignment could be achieved using a "constant" source of fluorescence. This system is depicted in figure 73a. It included a three way valve for the GC, so that once the components were aligned, the system would not need to be disturbed. As a result the gas lines were considerably extended, but this was definitely of secondary importance at that stage until actual GC sample separation became necessary.

The results obtained with this system were at first somewhat puzzling. The laser power being monitored after the IRTRAN cell showed a decrease while ethylene was passing through the cell (at 0.5-5% by volume flow rate). The thermocouple signal, on the other hand, with only nitrogen flowing, produced a rise in baseline. However, upon introduction of ethylene it decreased. Using the GC rather than the flowing system also produced inverted signals. (See figure 75.)
The source of the baseline, when the laser was directed through the cell containing only nitrogen, was not found to be due to thermal emission from the cell windows (or walls) being too hot, since cooling them with air streams on the outside surfaces did not affect the baseline.

If the sudden drop in baseline that was due to cooling then any gas which would pass through the cell would have the same effect: this hypothesis was tested by monitoring the baseline as two other gases were separately injected into the system. The same quantity of ethylene (a strong CO$_2$ laser absorber), propane (a weak absorber) and carbon dioxide (non absorbing of the CO$_2$ laser in its molecular ground state) was used. The ethylene produced the above mentioned sudden drops in the baseline as they emerged from the gc, while propane just slightly decreased the baseline and carbon dioxide didn't affect it at all.

The signals from the IR detector that were observed as baseline
due to radiation being scattered from within the cell; and as the ethylene absorbed this radiation, less of it was available for scattering.

3C,2. Static ethylene fluorescence source.

If the sudden decreases in baseline which were observed were indeed due to the reduction of scattered radiation then, absorption was occurring but fluorescence was not being observed. Since the signal from the gc was transient and the flowing nitrogen - ethylene mixture a little unstable (presumably due to the incomplete mixing), it was thought that a static gas volume would provide a better fluorescence source for further system alignment. A "stop flow" system was set up in which a known amount of ethylene was added to a known volume of nitrogen, and then kept undisturbed. Figure 73b shows a diagram of this system.

With the "stop flow" approach the gc line was replaced with a vacuum system so as to flush and evacuate the cell several times before preparing a volume of gases with a known concentration. In addition, provisions were included to clean and dry the nitrogen by using activated charcoal and silica gel, respectively. Another feature of this system was the water bubbler chamber, which served as an indication that the system had been brought back up to atmospheric pressure when the gas concentration was being prepared. The procedure followed for the preparation of known ethylene concentration was to first clean and flush the cell with nitrogen and evacuating it; this was followed by the injection of a known volume of ethylene and subsequently filling the rest of the volume with nitrogen, up to atmospheric pressure. (The volume of the static space was measured beforehand).
Since fluorescence depended on the power of the source at this point the laser power was increased by recoating the totally reflecting (back) mirror of the laser with gold; as a result the power was increased to 28 watts/cm² from 14-18 watts/cm².

Results obtained with the "stop flow" system were very similar to those obtained with the continuous flow set up, even with the increased laser power. The initial baseline drift (scatter) was larger and was attributed to the increased laser power; fluorescence was still not observed and gas impurities was disregarded as being a source of problems (fluorescence quenching) since the nitrogen was being scrubbed.

Various concentrations of ethylene were used and one could very discernibly observe the laser power being attenuated by the ethylene, and would remain so until the cell was evacuated. The detector was then mounted on an x-y-z adjuster and scanned across the cell window, or the focusing volume from the mirror when it was used, (figure 74c) but still no fluorescence could be observed, and only scatter from within the cell was recorded.

Since earlier workers in this group had recorded numerous infrared fluorescence spectra using the IR-10 instrument it was decided to use it to observe fluorescence. Another reason for using this instrument was that infrared energy dispersion would be necessary once the detection system was operating properly. Scanning the infrared region for each eluant was possible, though monitoring them at fixed wavelengths to be more probable using this system.

3. D. Cube cell - IR-10 Spectrophotometer.
The gas system used in the previous section was also used with the IR-10 (cf figure 73b), and only the optical system changed slightly as is shown in figure 74d. (The detector that was found in this instrument was not that reported in Katayama's work.149.)

With the grating turned to the 10.6 μm position (the major emission envelope of the laser) the cube gas cell, which was still on the x-y-z adjuster, was systematically scanned across the entrance slits to optimize the signal. However, this scatter emission signal (usually stronger than fluorescence at 10.6 μm) did not necessarily align the source of fluorescence reaching with the detector. However, as a first approximation this was useful. The stop flow method (with ethylene) was subsequently used to align the system more carefully.

The results, surprisingly, did not provide encouraging information regarding fluorescence. The background signals (observed as the baseline shift) at 10.6 μm were measured, and were seen to decrease with the presence of ethylene in the cell; also, when the infrared region was scanned, i.e., at wavelengths other than 10.6 μm the baseline returned to the recorder zero. At times it was thought that some fluorescence had been observed but upon repetition only background noise could be found. Varying the phase of the signal also produced a decrease of the baseline shift, suggesting that scatter was being measured. (Zero phase was set at 10.6 μm and with only nitrogen present in the cell; maximizing the signal under those conditions provided the equivalent of zero time delay between modulation of the source and the measurement of the signal.)

Since the adjustment of the components with the grating at 10.6 μm
optimized the scatter and resonant fluorescence signals coming from the IRTRAN cell, setting the grating at 10.4 µm would allow the system to be aligned only with fluorescence falling on the detector. This approach was tried repeatedly but still did not yield any of the desired results. (The laser power after passing through the cell was simultaneously recorded. It showed infrared absorption with ethylene while the gas system was static.)

Thus, it was thought that the system was not functioning as it was designed to, even when a still different thermocouple detector was placed in the IR-10 spectrophotometer. Consequently, further efforts with the same system were not thought to be warranted since considering the concentrations used, and the problems involved, it became apparent that the sensitivity of the detection system, as it was conceived, would be insufficient to use as a routine gc detector.

An explanation described more fully below is that the excited molecules with long lifetimes were deactivated by collision before they fluoresced. Hence, the signal was very small.

4. CONCLUSIONS.

Calculations by previous workers had shown that this method could possibly be used in remote sensing of atmospheric pollutants, even with the capability of ranging, i.e., determining the concentration in the air as a function of distance from the source. This was sufficient sensitivity in order to attempt to apply the method as a gc detector.

Efforts at this time proved to be unfruitful utilizing the described system, in which ethylene was being used because it had been
found to be a strong IR fluorescent compound. The fluorescence cell was
designed to be about one cubic centimeter at the fluorescence detection
interface, but proved to be inadequate for any fluorescence to be
observed, eventhough absorption of the laser beam did occur, as it was
routinely measured. Precautions were taken to eliminate possible
impurities in the gas system which would quench fluorescence of ethylene
within the cell. The laser power used as the excitation source was
thought to be sufficient (up to 14 watts/cm$^2$ chopped, before passing
through the IRTRAN window); various optical arrangements were also used
to provide an adequate system for IR-fluorescence as a new approach to
gc detection.

Lifetimes in the excited states have been previously measured, and
at the modulation frequency of 13 Hz ethylene was found to have a 70
millisecond lifetime at a 1% concentration at atmospheric pressure in
nitrogen; concentrations of about 1-10% were usually used in our
experiments, providing for long lifetimes in the excited state.
Consequently, it is thought that collisional deactivation of the ethylene
molecules, with themselves and with the cell walls was the overriding
factor in this system which prevented us from observing any
fluorescence. An impass was reached because two opposing factors were
important, the first, was the necessity to have a small volume cell in
order to maintain gc resolution of the peaks and secondly, the size of
the cell needed to be large for IR-fluorescence to be observed. As a
result, the gas fluorescence-cell as designed was inadequate for the use
as a gc detector, suggesting that considerable modifications were
needed before sensitivity levels compatible with gc detection could be
achieved.
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VITA

The author was born on November 20, 1952 in Santiago-Chile, of English father and French mother. The author finished his secondary education in Chile and came to the USA in January 1970. In April 1973 he obtained his Bachelor's degree. The remainder of that year was spent in Europe and returned to enroll in graduate school at LSU in January 1974. In August 1977 the author obtained his MSc degree minoring in Quantitative Methods (statistics). Circumstances were such that the author enrolled once again to pursue a Ph.D. degree in Analytical Chemistry in August 1977, for which he is now a candidate, having also diversified his studies to include a minor in Chemical Engineering.
EXAMINATION AND THESIS REPORT

Candidate: Peter L. H. Jowett

Major Field: Analytical Chemistry

Title of Thesis: A Study Of Metal Speciation Using A Two-Stage Electrothermal Atomizer. Laser IR Fluorescence As A GC Detector

Approved:

[Signatures]

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Date of Examination: November 23, 1982