1972

Determination of Selected Atmospheric Pollutants by Atomic Fluorescence and X-Ray Photoelectron Spectroscopy.

Yvon Elie Araktingi
Louisiana State University and Agricultural & Mechanical College

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The Louisiana State University and Agricultural
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DETERMINATION OF SELECTED ATMOSPHERIC POLLUTANTS BY ATOMIC
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A Dissertation

Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Doctor of Philosophy

in

The Department of Chemistry

by

Yvon E. Araktingi
B.S., American University of Beirut, 1965
M.S., Louisiana State University, 1968
August, 1972
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DEDICATION

To Elie and Blanche who gave without ever asking, for the betterment of their children.

To Patricia who made it a little easier and less lonesome.
"Experiment is the interpreter of nature. Experiments never deceive. It is our judgment which sometimes deceives itself because it expects results which experiment refuses."

Leonardo da Vinci
ACKNOWLEDGMENT

The author wishes to express his sincere appreciation and thanks to Professor J.W. Robinson, the director of this research, who was always available for guidance and encouragement especially during the darkest moments.

Considerable gratitude is due to Dr. N.S. Bhacca for his help in the E.S.C.A. studies and to Varian Associates for the use of their I.E.E. spectrometer.

In addition, the author wishes to thank the following members of the Louisiana State University, Chemistry Department technical staff: Messers R. Seab, G. Sexton, E. Keel, L. Rogge, R. Childree and especially C. Burlo for their assistance in the construction and operation of the instruments.

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ABSTRACT

The analytical techniques currently used for the determination of atmospheric pollutants involve the collection and concentration of the sample prior to analysis. These steps may introduce large errors due to contamination by reagents and apparatus and inefficiency of sample trapping. This research concerns the application of two analytical techniques to the direct determination of selected volatile and particulate pollutants.

PART I

A study was undertaken to determine the feasibility of utilizing atomic fluorescence spectroscopy for the direct determination of cadmium and mercury in the atmosphere. An instrument was constructed incorporating a flameless atomizer of graphite rods heated to around 1500°C, by induction with the field of a radio frequency generator. The air sample was passed over the rods and the reaction of oxygen with the carbon of the rods produces carbon monoxide. The carbon monoxide reacts with the compounds of mercury and cadmium present in the sample reducing them to the atomic state. The atoms were then introduced into the fluorescence cell where they absorbed light from a monochromatic source thus producing optically excited atoms. When a fraction of these excited atoms lost their energy by radiational processes, fluorescence light was emitted and detected at right angle to the source. The intensity of the fluorescence signal was directly proportional to the concentration of absorbing atoms, thus a quantitative determination was possible.
The above technique produced relatively low intensity fluorescence signals. When absorption was measured under the same experimental conditions it was found to be relatively high, thus indicating that enough atoms were reaching the fluorescence cell, but only a small amount was returning to the ground state via a radiational process, the bulk was then returning via a radiationless (or quenching) process.

The quenching effect of nitrogen and carbon monoxide on the fluorescence signals of mercury and cadmium was studied. This effect was found to be quite high under the operating conditions of the flameless atomizer used, thus explaining the low signals observed.

PART II

X-ray photoelectron spectroscopy was used to determine the chemical forms of several metallic and non-metallic elements present in airborne particulates.

The method essentially consisted in collecting an air sample on a filter paper, inserting the sample in the spectrometer and bombarding it by high energy X-rays. Electrons were then emitted from the various atoms present in the sample, their kinetic energy was measured and thus their binding energy was determined.

The binding energy of the electrons emitted was characteristic of the element from which the electrons came, moreover it was also a function of the chemical environment of the element in question. Several elements were observed in the spectrum of airborne particulates, these were oxygen, aluminum, iron, silicon, sulfur, lead,
chlorine, carbon, calcium and nitrogen. Detailed analysis was con­
ducted for nitrogen, lead and sulfur.
### LIST OF ABBREVIATIONS

The following abbreviations are used throughout this dissertation.

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<td>Å</td>
<td>angstrom</td>
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<tr>
<td>μ</td>
<td>micron</td>
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<td>mm</td>
<td>millimeter</td>
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<td>in.</td>
<td>inch</td>
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<td>a.u.</td>
<td>atomic unit</td>
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<td>ng</td>
<td>nanogram</td>
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<td>μg</td>
<td>microgram</td>
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<td>cubic centimeter</td>
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<td>hr.</td>
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<tr>
<td>mA</td>
<td>milliampere</td>
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<td>p</td>
<td>pressure</td>
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<td>v</td>
<td>volume</td>
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<tr>
<td>I.R.</td>
<td>infrared (spectroscopy)</td>
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<tr>
<td>U.V.</td>
<td>ultraviolet (spectroscopy)</td>
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- A = ampere
- eV = electron volt
- V = volt
- A.C. = alternating current
- K.C = kilocycle
- °C = degree centigrade
- °K = degree kelvin
- ° = degree
- I.D. = internal diameter
- O.D. = outside diameter
- N = normality
- exp = exponential
- % = percent
- fig. = figure
- w/v = weight per volume
- I_f = fluorescence intensity or radiance
- et. al = and others

**Additional Abbreviations:**

- ACS = American Chemical Society
- E.S.C.A. = electron spectroscopy for chemical analysis
- I.E.E. = induced electron emission
- N.M.R. = nuclear magnetic resonance (spectroscopy)
PART I

THE STUDY OF THE APPLICATION OF ATOMIC FLUORESCENCE SPECTROSCOPY TO THE DIRECT DETERMINATION OF MERCURY AND CADMIUM IN THE ATMOSPHERE
INTRODUCTION

"The environment has just been rediscovered by the people who live in it", this opening sentence of Barry Commoner in the "The Closing Circle" (1) adequately describes the present public attitude towards our environment.

Over the past decade, the concept of the earth as a "spaceship" has provided people with an awareness of the limited amount of resources and the complex natural relationships on which man depends for his survival. These realizations have been accompanied by concerns about the impacts that man's activities are having on the environment.

More recently serious questions have been raised about the effects on the ecosystem of systematic discharges of heavy metals such as lead, mercury, cadmium, chromium, etc. The toxicity of trace metals is well documented, lead poisoning or plumbism was known since biblical times, arsenic has long been used as an instrument of murder and suicide, mercurialism was prevalent among furriers and felters in the seventeenth century ("mad hatters disease"). Mercury is one of the most serious environmental contaminants among the heavy toxic metals. It is known to be a protoplasmic poison and thus is lethal to all forms of living matter. In general organo-mercury compounds are more toxic than elemental mercury or the inorganic compounds (2). Moreover inorganic compounds can be transformed to organic forms by the action of certain aquatic microorganisms (i.e., facultative anaerobes), this fact was realized only in 1966 (3, 4) and a detailed mechanism involved in the formation of methyl mercury compounds from
inorganic mercury was worked out (5, 6, 7, 8). However, it was not until 1970 that mercury pollution was recognized in the U.S. as a serious problem.

The inhibition of the sulfhydryl enzyme activities by the mercuric ion is a well-known phenomenon in biochemistry and the toxic effect of mercury compounds in biological systems may have been derived from the fact that mercury element binds with the thiol-group of the crucial enzyme proteins (9, 10). Mercury's toxicity is permanent. In addition, when fish, shellfish, birds or mammals containing mercury are eaten by other animals and man, the mercury may be absorbed and accumulated. It is interesting to note here that the world production of mercury in 1968 was 8,810 metric tons (11). The U.S. production was 1,000 metric tons in 1968 (11). From 1930 to 1970 the U.S. mined 31,800 metric tons, imported 39,600 metric tons and exported 1,820 metric tons, leaving 69,580 metric tons in the U.S. (12). Consumption during this 40 year period was 63,000 metric tons (12).

The major uses of mercury in the U.S. are electrical and electrolytic preparation of chlorine and caustic soda. The major sources of mercury in the atmosphere are mining and refining processes, electrical manufacturing, chlorine and caustic processing plants, burning of fossil fuels, agricultural uses, specialized industries (such as thermometer plants) and scientific laboratories.

As with mercury, very little was known about the fate and distribution of cadmium in the environment. It was known, however, to have a very long biological half-life in man and therefore tends to accumulate in the body. Estimates ranged from 10 to 25 years,
compared with about 30 days for methyl mercury. It was also known from industrial toxicology that cadmium can cause severe liver and kidney damage, pulmonary disease and death (1, 14, 15).

In 1960, the U.S. production of cadmium was 10.4 million pounds (11). Nearly all the cadmium produced was a by-product of zinc smelting. Recycling is virtually non-existent since only 0.2% of the U.S. production of cadmium was derived from reprocessing cadmium-containing scrap. Moreover, cadmium like mercury, does not degrade in the environment. U.S. consumption was 1.7 million pounds in 1965 (11) and all indications point to further increases in consumption in the future. In 1968, 4.1 million pounds of cadmium was emitted into the atmosphere in the U.S. (17), that is about one-third the production! Most emissions into the atmosphere fall into two general categories: disposal and metallurgical processing. Disposal includes incineration and recycling of ferrous scrap. Incineration of plastic products also adds to the cadmium discharged into the atmosphere. Metallurgical processing emits nearly as much cadmium to the air as disposal does. Roasting and sintering of ore release vast quantities of cadmium into the air. In 1968 as much as 0.7% of the cadmium discharged came from this source only. Smaller quantities come from a variety of processes such as the manufacture of batteries, alloys, plastics, pigments, as well as the use of certain fertilizers, fungicides, motor oils and rubber tires.

The toxicity of cadmium was recently investigated by researchers from the Stockholm's Karolinska Institute (18). The Swedish report showed that although the human body contains only 1 µg of cadmium at birth, a 30 year old (153 lbs.) man in the U.S. has a body burden
of about 50 mg, i.e., 10,000 times the amount at birth! Exposure to cadmium can cause liver, kidney, spleen and thyroid damage. The report also states that cadmium inhalation is more dangerous than ingestion, since only about 1% of ingested cadmium is absorbed by the body but as high as 50% could be absorbed from inhalation, this means that humans are physiologically much more sensitive to airborne cadmium contamination than to the low-level contamination of food and water. Cadmium has also been implicated in cardio-vascular disorders (21, 20) and cancer (21, 20) although the Swedish report emphasizes that there is no conclusive statistical evidence at the present time linking cadmium with these diseases.

Cadmium mimics mercury in its reaction with enzymes' sulfhydryl groups and zinc in its reactions with nitrogen and oxygen in the human body (23). It also affects the copper metabolism in ways which are yet unclear (23).

Since mercury's toxicity was recognized a long time ago, early methods were developed for its detection in the air. Some of these early methods were: electrolytic (24), colorimetric (25), optical absorption (26), selenium-sulfide detector (27), spot tests (28) and non-flame atomic absorption (29). More recently mercury was determined by the ring-oven technique (30), neutron activation analysis (31), X-ray fluorescence (32), electrochemically (33), by atomic absorption (34) and atomic fluorescence (35).

The recent mercury crisis of 1968-1970 prompted a great in­crease in the number of publications on the determination of mercury especially by non-flame atomic absorption (36-42) and non-flame atomic fluorescence (43-45). However, except for the selenium-sulfide
detector (27) and the detector described by Woodson (29) which were hindered by numerous interferences (i.e., water vapor, organic gases, sulfur compounds), none of the above techniques are able to perform the direct determination of mercury and its compounds in the atmosphere.

Cadmium has been determined spectrophotometrically (49) by atomic absorption (50), atomic fluorescence (51, 52), activation analysis (53), polarography (54), by ring oven technique (55), and by emission spectroscopy (56). Here again, none of the above techniques are capable of direct determination of cadmium and its compounds in the atmosphere.

In order to determine mercury and cadmium in the atmosphere by most of the above cited techniques, it is necessary first to collect and concentrate these metals in a suitable medium (filter paper or scrubbing solution). Large errors are introduced if contamination and/or adsorption of the metals by the walls of the containers occur (57). Scrubbing efficiency and recovery techniques are also a large source of errors. Moreover the lapse time between collection and analysis is often long for most of the above cited techniques and hence monitoring on a real time basis and identification of intermittent pollution sources is not possible.

In view of the shortcomings of the above techniques for the analysis of cadmium and mercury in the atmosphere, the objective of this research was to develop a method capable of determining directly cadmium and mercury in the atmosphere. Atomic fluorescence spectroscopy has been used quite successfully for the determination of cadmium and mercury (h4, h5, h6, h1, h2). Studies of the technique
were justified especially in view of its relatively high absolute detection limits for these metals \(10^6\) ng for cadmium (\(\text{Hg}\)) and \(10^7\) ng for mercury (\(\text{Hg}\)) in non-flame cells.

A. ATOMIC FLUORESCENCE AS AN ANALYTICAL TECHNIQUE

Atomic fluorescence spectroscopy is based upon the absorption of radiation by an atomic vapor thus producing optically excited atoms and the subsequent measurement of the radiation emitted when a fraction of these atoms lose their energy by radiational processes called atomic fluorescence.

The fluorescence of metal atoms in the vapor phase is a well known phenomenon first observed in sodium vapor enclosed in a glass bulb by R.W. Wood in 1903. Subsequent observations by physicists of atomic fluorescence in quartz cells are summarized and reviewed in two classical manuscripts by Mitchell and Zemansky and Pringsheim. It was not until 1924 that Nichols and Howes first reported observing atomic fluorescence in a bunsen flame. In 1925, Badger published a paper on the atomic fluorescence of thallium, magnesium, copper, silver, cadmium, mercury and sodium in a bunsen flame. Little work was done on atomic fluorescence from 1930 until 1956. In 1956 Alkemade and co-workers used flame atomic fluorescence as a method for investigating the fundamental physical and chemical processes that occur in flames. In 1961, Robinson noted weak fluorescence of the magnesium 2852 Å line in the study of the mechanism of elemental spectral excitation in flames. At the 1962 Spectroscopy Colloquium in Maryland, Alkemade described the use of atomic fluorescence as a means of measuring quantum yields for the sodium 5890 Å line, and indicated its possible use as an analytical
technique. In 1964 Winefordner and Vickers (66, 67) wrote their now "classical" papers on atomic fluorescence flame spectrometry as an analytical method. Since then atomic fluorescence has been used by many workers, and demonstrated for many elements (68, 69).

In atomic fluorescence spectroscopy, several types of fluorescence processes are possible, as shown in fig. 1. The fluorescence of greatest analytical interest is the resonance transition (as shown in fig. 1a), which results when the ground state atom is excited to an electronic excited state and then undergoes radiational deactivation to the ground state re-emitting radiation of the same energy which was absorbed, i.e., mercury 2537Å, cadmium 2288Å and cadmium 3261Å. The other three types are of minor interest to analytical chemistry. These include direct-line fluorescence (fig. 1b), which results when an atom is excited to a state which fluoresces to another state above the ground state, stepwise fluorescence (fig. 1c), which results when excitation is to a higher energy state which is deactivated to a lower excited state before emission and finally sensitized fluorescence, which results when an excited species (donor) transfers energy to another species (acceptor) which then fluoresces.

The mathematical relationships for the atomic fluorescence intensity have been worked out by Winefordner and co-workers (69-72), by Hoomayers (73) and by Alkemade (74).

If one considers a parallelepiped sample cell segment of fluorescence path length L, absorption path length 1 and height 1' (fig. 2) and makes the following assumptions:

a) Only a single isolated spectral line is considered.
Figure 1. Types of Atomic Fluorescence.

- Ground electronic level
- Excited electronic levels

Levels a, b, and c represent different transitions in the electron configuration.
Figure 2. Schematic Diagram of a Theoretical Atomic Fluorescence Cell Segment.
b) The spectral line is broadened only by Doppler and Lorentz broadening.

c) The cell region considered is uniformly illuminated by the source.

d) The fluorescence over the entire cell segment and the direction of the detector is imaged onto the monochromator.

e) The source area is larger than the absorption area (L x 1')

One can then derive the following expression (71) relating the radiance (or intensity) of the atomic fluorescence signal to the concentration of the ground state atoms in the light path for the case of a line source and low optical density (low atom concentration in the cell, which is the case for the work described here).

\[ I_F = \frac{\sqrt{\pi} \, e^{-\frac{\pi^2}{\Delta \lambda_D^2}} \, I_L \lambda_0 \phi (a, \sqrt{\pi}) \Theta}{c \, mc' \Delta \lambda_D \sqrt{\pi}} \, I_{L \lambda_0} \]  \hspace{1cm} (1)

or

\[ I_F = C I_L N_0 \]  \hspace{1cm} (2)

where

- \( C \): is a constant for a particular experimental set-up.

- \( \Omega_F \): is the solid angle over which fluorescence is measured, ster.

- \( \lambda \): Peak wavelength of emission of radiation, cm.

- \( f \): Oscillator strength for absorption transition, no units.

- \( \phi \): Quantum efficiency.

- \( I_L \): Integrated intensity of narrow line source, erg sec\(^{-1}\) cm\(^{-2}\).

- \( N_0 \): Concentration of atoms in lower level involved in transition, cm\(^{-3}\).

- \( \Delta \lambda_D \): Doppler half-width of atoms in flame, cm.

- \( c \): Speed of light, cm sec\(^{-1}\).

- \( a \): Damping constant (also known as a-parameter) no units.

- \( e \): Electron charge, esu.
\[ \lambda(a, \nabla) \text{: the Voigt profile integral is given by:} \]

\[ \lambda(a, \nabla) = \frac{a}{\pi} \int_{-\infty}^{+\infty} \exp \left( -y^2 \right) \frac{dy}{a^2 + (\nabla-y)^2} \quad (\ast) \]

where

\[ a = \frac{\Delta L}{\Delta \lambda_D} \quad (h) \]

and

\[ \nabla = \frac{\Delta L}{\Delta \lambda_a} \quad (i) \]

where

- \( \Delta L \) = Lorentz half-width of atoms in cell, cm.
- \( \Delta \lambda_a \) = Absorption line half-width of atoms in cell, cm.
- \( \Delta \lambda_s \) = Source line half-width, cm.

From equation (\( \ast \)) we can see that for a particular set-up the fluorescence radiance (also known as fluorescence intensity) is directly proportional to the intensity of the radiation source and the number of atoms in the light path which can absorb.

Since the sensitivity of atomic fluorescence depends directly upon the atomic concentration of the species of concern, a variety of techniques have been considered to increase the efficiency of the atom reservoir. Flames, which have been used so far may not be efficient due to incomplete solute vaporization, compound formation of some elements (zirconium, silicon, boron, etc.) with flame gas products, and significant ionization with other elements (e.g., sodium, potassium, rubidium, cesium, etc.).

Recently a "rediscovery" of non-flame cells for atomic
fluorescence produced a great increase in the number of publications in the analytical literature.

The simplest non-flame atom reservoirs have been based on the L'vov graphite furnace (7\textsuperscript{a}) in an inert atmosphere. Variations of the graphite furnace for atomic fluorescence have been described by Massman (7\textsuperscript{b}), Winefordner (7\textsuperscript{c}), West and co-workers (77). However none of these methods is applicable to the direct determination of metals in the atmosphere.

Recently a flameless atomic absorption technique was developed in this laboratory (7\textsuperscript{a}, 7\textsuperscript{c}, 7\textsuperscript{d}), which would determine lead, mercury and cadmium and their compounds directly in the atmosphere and with very high sensitivity. The technique consists mainly in passing a slow moving airstream containing the metal to be determined over carbon rods heated to around 1100-1200 \textdegree C by induction with a radio frequency field. The carbon reacts with the oxygen of the atmosphere thus producing carbon monoxide which reduces the metal to the atomic state. The atoms then flow into a heated absorption tube maintained in the light path and their absorption of resonant radiation is measured.

In the present investigation we undertook the task of modifying the above cited technique from the absorption mode to the fluorescence mode in order to investigate its applicability for the direct determination of mercury and cadmium in the atmosphere.
A. DESCRIPTION OF THE EQUIPMENT

1. Components

The data reported were collected with instrumentation assembled in our laboratory partly from commercially available equipment and partly from constructed equipment. Fig. 3 shows a block diagram of the apparatus.

a. Monochromator

A one-half meter Techtron model MI (AA3) Ebert grating monochromator with adjustable slit was used.

b. Detector

An IP28 R.C.A. photomultiplier.

c. Amplifier

Techtron A.C. unit (AA3).

d. Radiation sources

For mercury: Pen lamps from Ultra Violet Products Inc., powered with 0.33A, 110 V, A.C. transformers. For cadmium: An Osram lamp powered by a Perkin-Elmer osram-type power supply that could provide 500 to 1100 mA was used to excite fluorescence, and a Perkin-Elmer Intensitron hollow-cathode lamp was used to monitor the absorption signal powered by a Techtron AA3 hollow-cathode power supply.

A lamp housing model LH-151N from Schoeffel Instruments Corp. equipped with an adjustable speed blower, double quartz condenser and a focusing sleeve was used to house the light source used to excite fluorescence.
Figure 3. Block Diagram of the Instrument used for the Determination of Mercury and Cadmium.

1. Gas tank 7. Sample injection system 13. Source power supply
e. **Recorder**

A Beckman 10005, 10 in. strip chart recorder.

f. **Radio-frequency generator**

A Lepel high-frequency induction unit (250-450KC) model number T-5-3-KC-E-SW was used to heat the carbon rods of the atomizer.

g. **Miscellaneous**

Tanks of compressed air, argon and nitrogen (pre-purified grade) were obtained locally (Big T Co.). The carbon monoxide tank was ultra-high purity grade from Air Products Co. Tank regulators were all double stage from Victor Equipment Co. and The Matheson Co. Gas flows were monitored by flowmeters from The Matheson Co., equipped with tubes number 602 and number 610, and number 150-microflow valves.

Quartz tubing joints and optical flats (suprasil number 2) were used in the construction of the cell; they were from Amersil Inc. Quartz lenses were furnished with the Techtron AA3 instrument.

Resistance wire used to wrap the cell was obtained from the Kanthal Co. type Al, 21 gauge and powered by powerstats from the Staco Inc. An air compressor equipped with a precision thermostat and water circulation system from Brinkmann Instruments Co. was used in conjunction with a Sargent thermonitor model S-N and a Sargent thermistor probe, for the thermostated bath around the mercury pool.

A rotary type pressure and vacuum pump from Sargent was used to draw air samples into the cell and also to evacuate the system when needed.

A Leeds and Northrup potentiometer was used in conjunction with a chromel-alumel thermocouple which reference junction was immersed in an ice-water bath (0°C).
A Coleman model MAS-50 mercury analyzer system was used to determine the mercury concentration in the fluorescence cell as described later. Reagents for the mercury analysis were obtained from Coleman Instruments.

The gas tight syringe used in the direct injection calibration method (described later) was from the Hamilton Co.

2. Construction of equipment
   a. The fluorescence cell

   The fluorescence cell shown in fig. 4 was constructed from 25 mm I.D. quartz tubing in the shape of a cross. This design was chosen because one can monitor the fluorescence and absorption signals without having to displace the cell or the radiation sources. A compromise in choosing the length of the sides of the cell was arrived at in order to secure maximum heating efficiency and minimum self-absorption of the fluorescence signal. The bilateral sides were 1 1/2 in. each in length and the top central side, where the exciting radiation fell, was 1 in., the lower central side or stem was 12 in. long and had a quartz male standard taper joint size 29/42 sealed on the end. The female part of this same joint had the gas-sample inlet tube and a chromel-alumel thermocouple to monitor the cell temperature at the fluorescence zone.

   The exhaust port was a 10 mm quartz tube situated above the center part of the cell and had a quartz socket joint on the end which joined to a ball joint attached to neoprene tubing and to a flow-meter, from there the exhaust gases were vented directly under the hood or through the air pump.

   The stem portion of the cell was positioned inside the radio
frequency coil. The induction coil was constructed of 10 turns of 1/8 in. O.D. copper tubing. This particular number of turns gave the best inductance match with the loading coil of the generator. Water was continuously passed through the copper coil in order to hold its temperature below the melting point of copper. In order to easily insert the carbon rods, an 11 in. 1/8 mm O.D. quartz tube was used to hold the eight 1/16 in. x 1/16 in. carbon rods and was slipped into the cell stem.

The Suprasil windows on the ends of the cell were heat sealed with minimum distortion to their optical transmission.

The cell was first wrapped by moistened asbestos paper, when this dried the cell was then wrapped with Kanthal A1, gauge number 22, resistance wire which was previously coiled in the machine shop. Alternating turns of resistance coil and asbestos string were wrapped. Several layers of asbestos tape were then added and moistened asbestos paper was laid over all this to insure adequate heat insulation. The leads of the resistance coil were attached to an 1A powerstat transformer. The maximum temperature attained was 270°C as measured by the referenced chromel-alumel thermocouple inside the cell.

When the side stem was not heated by radio frequency induction, as in the modified system to be described later, it was also wrapped with Kanthal A1, 21 gauge coil over its total length.

b. Gas sample inlet system

The apparatus shown in fig. 5 was constructed of Pyrex glass and a minimum amount of neoprene tubing, especially between the gas tanks and the fluorescence cell, to minimize any diffusion of
air into the system.

Gases from the tanks (argon and nitrogen or carbon monoxide) were first monitored by precision flowmeters equipped with microvalves. They were then passed over heated copper catalyst tubes and then over drying columns and finally over tubes filled with activated charcoal, the function of all of which will be described in the following section. The gases were then passed through cold traps, packed with glass wool and immersed in dry-ice acetone bath (for the argon and nitrogen lines) and liquid nitrogen bath (for the carbon monoxide line). The gases were then mixed in a T shaped tube filled with glass wool before passing over the sample injection system and into the fluorescence cell. The system was designed so as to also permit direct passage of the gases over the injection system, thus bypassing the purification train and also the direct passage of the gases or ambient air into the fluorescence cell, thus bypassing the sample injection system.

(1) **Gas purification train**

Early in the search it was found (by gas chromatography and mass spectrometry analyses) that the gases used, especially nitrogen, contained low levels of impurities such as oxygen which could interfere with the quenching studies to be undertaken, therefore, it was deemed necessary to purify the gases. This was done by passing them over heated (210°C) copper catalyst (Cu-2-0°C T from the Harshaw Chemical Co.) contained in a 17 in. long, 2 in. O.D. Pyrex tubes wrapped with resistance coil, insulated by asbestos tapes and connected to the terminals of A powerstats. Since the catalyst was furnished in the form of copper oxide, it had to be
Figure 5. Gas Inlet System.

- Lead to powerstat
- Stopcock
- Drying tube
- Activated charcoal tube
- Flow meter
- To fluorescence cell
- Needle valve
- Purifying tube
- Gas tank
- Tank regulator
- Asbestos sheath
- Cold trap
- Dewar flask
- To fluorescence cell
- Gas inlet
reduced by passing hydrogen over it at about 500°C. The purifying tubes were designed so as to be able to regenerate the catalyst during operation without disconnecting them. Since the reaction of hydrogen with copper oxide produced water vapor, it was necessary to use drying columns (Pyrex tubes 12 in. long, 2 in. O.D.) filled with Drierite in order to prevent any water vapor contamination of the fluorescence cell. The activated charcoal tubes (12 in. long, 2 in. O.D. Pyrex tubes) were used in order to prevent any metallic impurities present in the gases or generated in the purifying tubes from reaching the fluorescence cell.

(2) Sample inlet system

In the case of mercury, a small amount of the metal was placed in a porcelain boat which was sealed inside a polyethylene tube and immersed in a constant temperature bath (see fig. 6). The constant temperature bath consisted of a covered and insulated plastic cuvette filled with distilled water. The water temperature was controlled by two independent systems: One system consisted of copper tubing in the form of coils immersed in the water bath inside of which a water-antifreeze solution was circulated by means of an air compressor equipped with a high precision thermostat, the second system consisted of a light bulb partly immersed in the water bath and connected to a Sargent thermonitor system. The temperature of the light bulb filament was monitored by a thermistor probe immersed also in the water bath and attached to the thermonitor system. The temperature of the water bath and thus the mercury pool was read by means of a Beckman thermometer and could be maintained to ±0.05°C for long periods of time by slowly stirring the water with a mechanical stirrer.
Figure 6. Mercury Reservoir Diagram.
electrically powered.

In the case of cadmium, a solid injector had to be constructed since no volatile cadmium compounds were available. This was essentially a quartz tube of 10 mm O.D. wrapped with alternating turns of asbestos string and Kanthal Al, 21 gauge resistance wire. Several layers of asbestos tape were added for insulation. This heater was sealed to the female part of the stem of the fluorescence cell (fig. 7). The leads of the resistance heater were attached to an 8A powerstat transformer. The temperature of this solid injector was calibrated against powerstat reading by means of a thermocouple inserted about the middle section of the tube and while the system was in operation. Cadmium in the form of a piece of thin foil was introduced to about the middle of the injector by means of a small porcelain boat. The temperature of the injector was maintained constant during operation and was found so, by monitoring the cadmium absorption signal at 2288$\text{Å}$ as explained later in the section under cadmium studies.

c. Optical system

A view of the optical system is shown in fig. 8. The radiation from the source was condensed by a concave reflecting mirror and a double plano-convex quartz lens system (in the Schoeffel lamp housing) and focused into the cell through window number 1. The fluorescence light was collected from the cell at a ninety degree angle from the exciting light through cell window number 2 and focused onto the monochromator slit by a 2.5 in. focal length double convex quartz lens of 1 1/4 in. diameter.

When the absorption signal was monitored, the light source was
Figure 7. Solid Sample Injection Furnace Diagram.

- Lead to powerstat
- Asbestos paper
- Asbestos sheath
- Resistance coil
- Asbestos string
- 10 mm Quartz tubing
- 29/42 Quartz joint
Figure 8. Optical System Diagram.

Light source ———— Double convex quartz lens ———— Fluorescence cell ———— Window number 2

Plano convex lens ———— Reflecting mirror ———— Window number 1

Light source ———— Window number 3 ———— Monochromator slit
placed in front of the cell window number 1 and focused into the cell by a 2.5-in. focal length double convex quartz lens.

B. PRELIMINARY INVESTIGATION

Early in this search, a preliminary and qualitative study was undertaken to determine the scope and applicability of the technique. Several metals were investigated, i.e., lead at 2274Å and 4052Å, copper at 3248Å, zinc at 2139Å, cadmium at 2224Å, thallium at 3776Å and mercury at 2537Å. Trace concentrations of the metal atoms were introduced into the cell via the solid injection system described in a preceding section.

This preliminary investigation showed that although a strong absorption signal was observed for each of the above studied metals, the corresponding fluorescence signal was relatively weak. Since the light sources used (Osram and Phillips vapor discharge lamps, 1000 watts xenon-mercury arc, mercury pen lamp) were intense enough to excite the fluorescence spectrum under otherwise similar conditions, the above results then strongly suggested that although enough atoms in the ground state were reaching the light path, a relatively large number of atoms in the excited state were returning to the ground state via a non-radiative deactivation process, thus appreciably decreasing the radiance of the fluorescence signal. The above deactivation mechanism is quite probable if one considers that the main species in the cell beside the atoms of the element in question are molecules of carbon monoxide (from the reaction of the carbon rods with the oxygen of the air at 1100-1200°C) and nitrogen (from the air which passes unchanged over the carbon rods). These two molecular species are well-known and characterized as strong
fluorescence quenchers. However most of the previous work done on the fluorescence quenching abilities of carbon monoxide and nitrogen was undertaken under low pressure systems (59, 81-84) or in the flame (85-89). We therefore decided to investigate this quenching effect in our particular set up and at atmospheric pressure which is the usual manner the technique is to be utilized in practice. In order to do so, the system had to be modified.

A simpler system was designed whereby the metallic atoms were carried into the fluorescence cell by argon which is known to be an extremely weak fluorescence quencher (59, 81-89), a fluorescence signal was then recorded and adjusted to 100 arbitrary units. Increasing concentrations of nitrogen were then introduced and the decrease of the fluorescence signal was studied under various cell temperatures, the same was done for carbon monoxide. In this modified system no carbon rods were employed.

Since mercury vapor already exists in the atomic state, no problem was encountered in its atomization, as for cadmium it was easily atomized in argon atmosphere using a piece of thin cadmium foil and the solid injector described earlier. The radio frequency coil thus eliminated, the stem of the cell was heated by resistance coil when cadmium was studied.

Later on we shall describe the results obtained for the above two systems studied (cell without carbon rods atomizer and cell with carbon rods atomizer) for the two metals investigated: mercury and cadmium.
C. STUDIES ON THE DETERMINATION OF MERCURY

1. Equipment

a. Mercury light source

A low-pressure Philips 60W mercury lamp was first used, however, its output at 185.2Å was not enough to excite a strong fluorescence signal. A pen lamp (arc discharge lamp) powered by an A.C. transformer under the same experimental conditions produced a more intense signal at 253.7Å which excited a relatively stronger fluorescence signal. It was therefore used during this investigation. It was found, however, that the intensity of the pen lamp at 253.7Å decreased appreciably with time and was not stable. This was attributed to Doppler and collision broadening and self-reversal of the emitted resonance line which occurred at high temperature and also to the absorption of ultraviolet light by the ozone generated by the lamp around it. It was found that by gently blowing air around the lamp, its signal increased and remained stable for long periods of time as shown in fig. 9 (table I). The air had two beneficial effects on the lamp; first it cooled its wall thus decreasing somewhat the collision and Doppler broadening, and secondly it dispersed the absorbing ozone in front of its light path.

A second and similar mercury pen lamp was used to study the absorption signal as described previously.

b. Mercury sample reservoir (pool)

Metallic mercury was kept in a small porcelain boat inside a sealed polyethylene tube which was immersed in the thermostat bath previously described. The temperature of the bath was kept at
Figure 9. Intensity Versus Time for the 2537 Å Line of the Mercury Source.
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<th>Intensity (arbitrary units)</th>
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4.4°C ± 0.0°C and all the data reported were obtained at this setting unless otherwise specified. Accurate control of the mercury pool was necessary to insure a constant mercury concentration in the fluorescence cell. The above temperature used was arrived at as a compromise between the amplification level which gives a working signal with maximum signal to noise ratio and a minimum concentration of atoms so as not to cause quenching by self-absorption or "imprisonment" of fluorescence radiation in the cell.

... Operating parameters of the instrument

The following instrumental parameters were optimized to give a stable fluorescence signal with least amount of noise:

a. Detector high voltage
b. Amplifier gain
c. Monochromator slit width
d. Gas flow rate
e. Temperature of the cell
f. Radio frequency power

a. Detector high voltage

The high voltage on the IP25 tube was maintained at 950 V, except when otherwise indicated.

b. Amplifier gain

The coarse gain-control was maintained at position 5 on the Techtron AA2 amplifier, except when otherwise indicated. The signal could be further adjusted by manipulating the fine gain control knob.

c. Monochromator slit width

The slit width for the fluorescence measurements was
maintained at 300 µ and for the absorption measurements at 100 µ, except when otherwise indicated.

d. **Gas flow rate**

The optimum flow rate was found to be 400 cc/min. This flow rate was used throughout. Whenever two gases were mixed it was always insured that the total flow passing inside the cell was 0.6 cc/min as monitored by the flowmeter on the exhaust port.

e. **Cell temperature**

The cell temperature could be varied from room temperature (2°C) to around 50°C which was the maximum attainable temperature. The cell was operated always at just above room temperature, i.e., 50°C and was heated up to 70°C, since operation for long periods of time at higher temperature tend to shorten the life of the resistance coil and operation at lower than 50°C caused temperature fluctuations inside the cell. The cell temperature was controlled to within ±1°C.

f. **Operating conditions of the radiofrequency generator**

- Oscillator filament voltage: 12V
- Grid current: 0.9A
- Plate current: 1.4A
- Power control current: 4mA

The above conditions were found to give the maximum energy transfer between the tank coil and the load coil, thus producing the maximum attainable temperature of the carbon rods (1200°C as observed with an optical pyrometer).

Whenever the above experimental conditions (Detector high voltage, Amplifier gain, Monochromator slit width, Gases flow rate, Cell temperature) were altered, the new set of conditions are shown in
the respective tables and graphs pertaining to those conditions.

D. STUDIES ON THE DETERMINATION OF CADMIUM

1. Equipment

a. Cadmium light source

An Osram discharge lamp was used to excite the fluorescence, it was powered by a Perkin-Elmer-Osram lamp power supply at 1100 mA. The lamp envelope was punctured in order to allow excitation by the 2288 Å line.

The intensity of the lamp as a function of time over a 60 min. period is shown in fig. 10 (table II) for the 2288 Å line.

The absorption signal was monitored by a Perkin-Elmer Intensition hollow cathode, powered by the Techtron AA hollow cathode power supply. The lamp current was maintained at 8 mA. The emission signal was found to be stable at this current for long periods of time.

b. Cadmium injection system

The solid injector described previously was used. Its temperature was maintained at 250°C by the use of two powerstats in series, one for setting the voltage and the other to make final fine adjustments to the voltage. The above temperature was found to provide adequate cadmium concentration to give a working and stable signal with minimum amount of noise (see calibration section later).

The side stem of the fluorescence cell was wrapped with resistance wire, when the radio frequency heating was not used. Temperature of the side stem was maintained at 400°C in order to avoid any cadmium condensation.

2. Operating parameters of the instrument

The following instrumental parameters were optimized to
Figure 10. Intensity Versus Time for the $^{228}$R Line of the Cadmium Source.
TABLE II

INTENSITY OF CADMIUM LAMP AS A FUNCTION OF TIME AT 2288Å

Slit width: 100 μm, High voltage on detector: 600 V,
Amplifier gain: 8.

<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>Intensity (arbitrary units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>80.2</td>
</tr>
<tr>
<td>10</td>
<td>79.8</td>
</tr>
<tr>
<td>15</td>
<td>80.0</td>
</tr>
<tr>
<td>20</td>
<td>80.1</td>
</tr>
<tr>
<td>25</td>
<td>79.7</td>
</tr>
<tr>
<td>30</td>
<td>80.0</td>
</tr>
<tr>
<td>35</td>
<td>79.8</td>
</tr>
<tr>
<td>40</td>
<td>80.2</td>
</tr>
<tr>
<td>45</td>
<td>80.2</td>
</tr>
<tr>
<td>50</td>
<td>80.1</td>
</tr>
<tr>
<td>55</td>
<td>79.8</td>
</tr>
<tr>
<td>60</td>
<td>79.8</td>
</tr>
<tr>
<td>65</td>
<td>80.1</td>
</tr>
<tr>
<td>70</td>
<td>80.0</td>
</tr>
<tr>
<td>75</td>
<td>80.0</td>
</tr>
<tr>
<td>80</td>
<td>80.1</td>
</tr>
<tr>
<td>85</td>
<td>79.9</td>
</tr>
<tr>
<td>90</td>
<td>79.9</td>
</tr>
</tbody>
</table>
give a stable fluorescence signal with least amount of noise:

a. Detector high voltage

b. Amplifier gain

c. Monochromator slit width

d. Gas flow rate

e. Cell temperature

f. Radio frequency power

   a. **Detector high voltage**

      The high voltage on the IP2½ tube was maintained at 10 V, except when otherwise indicated.

   b. **Amplifier gain**

      The coarse gain control on the amplifier was maintained at position 10, except when otherwise indicated. The signal could further be adjusted by manipulating the fine gain control knob.

   c. **Monochromator slit width**

      The slit width on the monochromator was maintained at 00 μ for the fluorescence measurements and at 100 μ for the absorption measurements, except when otherwise indicated.

   d. **Gas flow rate**

      The total flow rate of gases passing through the cell was maintained at 200 cc/min.

   e. **Cell temperature**

      The cell temperature was varied from 0°C to 15°C. The lower limit was necessary in order to prevent any cadmium condensation on the cell windows.

   f. **Operating conditions of the radio frequency generator**

      Same as for the mercury studies previously described.
RESULTS

A. MERCURY STUDIES

1. Modified system without radio frequency heating

The results reported below are those for the simple system described earlier in which no carbon rods or radio frequency heating was used. Purified argon was passed over a thermostated mercury pool at 200 cc/min. and into the fluorescence cell. The signal was adjusted to 100 arbitrary units, various amounts of purified nitrogen were then introduced into the cell and the fluorescence signal recorded, the same was done with carbon monoxide. The above experiments were undertaken at various cell temperatures.

a. Stability of the fluorescence and absorption signals

Fig. 11 shows a plot of $I_f$ (fluorescence radiance in arbitrary units) versus time for the mercury 248.3Å in pure argon atmosphere at cell temperature 50°C. The noise level was one arbitrary unit (noise level 1%).

Fig. 12 (table III) shows a plot of absorbance versus time for the 253.7Å mercury line in pure argon at cell temperature 30°C. The absorption signal was found to be the same in pure nitrogen and pure carbon monoxide and in various mixtures of these two gases with argon.

Since the cooled source was previously found stable (fig. 9), the above results indicate that a fairly constant amount of mercury was being introduced into the cell over long periods of time.

b. Titration methods

In order to have an idea of the amount of mercury
Figure I. Fluorescence Radiance Versus Time for Line of Mercury in Pure Argon at 70°C.
Figure 1. Absorbance Versus Time for Mercury in Pure Argon at 0°C.
<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.125</td>
</tr>
<tr>
<td>20</td>
<td>0.128</td>
</tr>
<tr>
<td>30</td>
<td>0.124</td>
</tr>
<tr>
<td>40</td>
<td>0.125</td>
</tr>
<tr>
<td>50</td>
<td>0.124</td>
</tr>
<tr>
<td>60</td>
<td>0.127</td>
</tr>
</tbody>
</table>
introduced into the cell two calibration methods were used.

The first we will label: Determination by the Coleman MAS-50 mercury analyzer and the second, determination by direct injection of mercury vapor.

(1) Determination of the mercury in the cell by the Coleman MAS-50 mercury analyzer

(a) Principle of the method

The Coleman MAS-50 mercury analyzer system (see diagram, fig. 13) is essentially based on the Hatch and Ott procedure (1,7). Basically the system works as follows: 100 ml of the sample is treated with nitric and sulfuric acid in the presence of potassium permanganate to oxidize all the mercury present to the mercuric \((\text{Hg}^{2+})\) form. The excess permanganate is reduced with hydroxylamine hydrochloride and then the mercury is reduced to the metallic form with stannous chloride. A bubbler is placed in the reduced mercury solution. A pump circulates the air trapped in the system through the solution and the air evaporates the mercury and carries it through the absorption cell. The mercury vapor, which is in the atomic form, absorbs the \(2537\AA\) radiation emitted from the light source. The change in energy transmitted through the cell is detected with a ultraviolet sensitive phototube. A narrow band-pass filter in front of the phototube allows only the \(2537\AA\) radiation through.

(b) Standard mercury solutions

Standard mercury solutions in the range of 1 to 4 \(\mu\)g were prepared from a stock solution (100 \(\mu\)g/ml) of mercuric chloride in 1 N nitric acid (Coleman mercury free, ACS grade) prepared from distilled-deionized water. The calibration curve for
1. Source power supply
2. Ballast
3. Mercury lamp
4. Absorption cell
5. Pump
6. BOD bottle and bubblers
7. Filter
8. Photo house
9. Photo amplifier
10. 100% T adjustment
11. % T adjustment
12. Recorder
13. Memory
14. Buffer amplifier
15. Scale selector
16. Meter readout

Figure 17. Block Diagram of the Coleman MAS-50 Mercury Analyzer.
the range $1$ to $\frac{1}{4}$ $\mu g$ is shown in fig. 14 and the data tabulated (table IV). The precision for the $1$ $\mu g$ standard analysis, which is typical of the rest, is shown in table V.

(c) **Samples collection**

Purified argon at a flow rate of 200 cc/min. was passed over the thermostated mercury pool into the cell and then collected at the exhaust port in two BOD bottles in series equipped with glass-fritted bubblers and each containing the following:

- 20 ml of 5.6 N mercury free, ACS grade, nitric acid
- 5 ml of 18 N sulfuric acid, ACS grade, mercury free
- 2 drops of 5% w/v, potassium permanganate, ACS grade
- 88 ml of distilled-deionized water
- glass beads

Samples were collected over periods of 20 to 60 min. At the end of the collection period the bottles were disconnected and the following reagents were added just prior to analysis:

- 5 ml of 1.5% hydroxylamine hydrochloride solution (ACS grade)
- 5 ml of 10% stannous chloride reagent, (ACS grade)

(d) **Mercury concentration in the cell**

The results for various gas mixtures, at various cell temperatures are tabulated (table VI). Column 5, in table VI, was computed by taking into account the cell volume which was 203.3 ml. No mercury was detected in the back-up bottles for all the runs made. The average value for the mercury concentration in the cell at any one time was found to be 0.061 $\mu g$ (61 ng), when the mercury pool temperature was maintained at $4.5^\circ C$. 
Figure 14. Calibration Curve for Mercury Determined by the Coleman MAS-50 Analyzer.
TABLE IV
DATA FOR THE CALIBRATION CURVE OF MERCURY DETERMINED
BY THE COLEMAN MAS-50 ANALYZER

<table>
<thead>
<tr>
<th>Mercury concentration (µg)</th>
<th>Absorbance (average of 6 values)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.177</td>
</tr>
<tr>
<td>1.5</td>
<td>0.265</td>
</tr>
<tr>
<td>2</td>
<td>0.352</td>
</tr>
<tr>
<td>2.5</td>
<td>0.469</td>
</tr>
<tr>
<td>3</td>
<td>0.553</td>
</tr>
<tr>
<td>4</td>
<td>0.735</td>
</tr>
</tbody>
</table>
### TABLE V

**PRECISION OF THE DETERMINATION OF THE 1 \( \mu \text{g} \) MERCURY STANDARD SOLUTION BY THE COLEMAN MAS-50 ANALYZER**

<table>
<thead>
<tr>
<th>Run number</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.178</td>
</tr>
<tr>
<td>2</td>
<td>0.172</td>
</tr>
<tr>
<td>3</td>
<td>0.174</td>
</tr>
<tr>
<td>4</td>
<td>0.177</td>
</tr>
<tr>
<td>5</td>
<td>0.176</td>
</tr>
<tr>
<td>6</td>
<td>0.182</td>
</tr>
</tbody>
</table>

Average = 0.177  
\( \sigma = 0.001 \)
<table>
<thead>
<tr>
<th>Gas composition</th>
<th>Cell temperature (°C)</th>
<th>Sample collection time (min.)</th>
<th>Total mercury concentration in sample (µg)</th>
<th>Concentration of mercury in the cell at any one time (µg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure Argon</td>
<td>30</td>
<td>20</td>
<td>1.23</td>
<td>0.058</td>
</tr>
<tr>
<td>Pure Argon</td>
<td>30</td>
<td>30</td>
<td>1.85</td>
<td>0.061</td>
</tr>
<tr>
<td>Pure Argon</td>
<td>30</td>
<td>60</td>
<td>3.62</td>
<td>0.063</td>
</tr>
<tr>
<td>Pure Argon</td>
<td>350</td>
<td>30</td>
<td>1.72</td>
<td>0.060</td>
</tr>
<tr>
<td>Pure Argon</td>
<td>800</td>
<td>30</td>
<td>1.75</td>
<td>0.061</td>
</tr>
<tr>
<td>50% Argon - 50% Nitrogen</td>
<td>30</td>
<td>30</td>
<td>1.76</td>
<td>0.061</td>
</tr>
<tr>
<td>Pure Air (from compressed air tank)</td>
<td>30</td>
<td>30</td>
<td>1.76</td>
<td>0.061</td>
</tr>
</tbody>
</table>

Average = 0.061
\[\sigma = 0.002\]
(2) **Determination of the mercury in the cell by direct injection procedure**

(a) **Principle of the method**

Air saturated with mercury vapor at a known temperature was injected through a rubber septum by means of a gas-tight syringe into the argon stream flowing in the cell and bypassing the mercury reservoir. The absorption signal (peak height) was recorded. By varying the amount of air injected, the final mercury concentration introduced was varied. The absorption signal from the mercury reservoir in the system was then recorded. By constructing a calibration curve from the injection data, the mercury concentration in the cell at any one time was calculated.

(b) **Mercury vapor standards**

A few drops of triple distilled mercury were poured in glass bottles sealed with rubber septums and kept in a thermostated water bath at 20°C until equilibrium was reached and the air in the bottles was saturated with mercury vapor. Known volumes of air were then withdrawn by means of a gas-tight syringe from the containers and injected into the argon stream flowing in the system as described above. Knowing the container temperature, the concentration of mercury of the air standards could be calculated, since the vapor pressure of mercury at 20°C is known to be $12 \times 10^{-4}$ mm (90). It is easily found, assuming ideal gas behavior and complete saturation, that one cubic centimeter of air from the bottles contains $13.1$ ng of mercury. After each withdrawal of air from the container, air from the room was allowed to enter the container in order to re-establish atmospheric pressure conditions and
the next withdrawal was made from a different bottle in order to give the previous bottle enough time to reach saturation.

(c) Calibration curve

Fig. 15 (table VII) shows the calibration curve for the injection technique over the range of 26 to 79 ng of mercury. Table VIII shows the precision of the 65 ng injection which is typical of the rest. At cell temperature 30°C and mercury reservoir temperature 4.5°C, the concentration of mercury in the cell at any one time was found to be 67 ng (table IX), a little higher value than that found by the previous calibration method, which is expected since possibilities of mercury loss are diminished in the direct injection method.

At higher cell temperatures (350°C and 800°C) the absorption signal from injected mercury standards was appreciably decreased, the same effect was also observed for the mercury signal from the mercury reservoir in the system, this effect will be discussed later.

c. Effect of increasing nitrogen and carbon monoxide concentration on the fluorescence signal in argon at 30°C

Upon mixing relatively low amounts of purified nitrogen gas (1%, 3%, 5%, 8%) with the purified argon stream entering the fluorescence cell at 30°C, the fluorescence radiance was found to decrease rapidly as shown in fig. 16 (table X). Fig. 17 (table XI) shows a plot of the ratio of the fluorescence radiance in pure argon over the fluorescence radiance in argon-nitrogen mixtures [defined as $1/Q$ (see Discussion)] versus percentage nitrogen added. In this nitrogen concentration range the curve is linear. At higher nitrogen concentrations (above 5%), the decrease in fluorescence radiance is
Figure 15. Calibration Curve for Mercury Determined by the Direct Injection Method.
<table>
<thead>
<tr>
<th>Mercury concentration (ng)</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>0.070</td>
</tr>
<tr>
<td>39</td>
<td>0.086</td>
</tr>
<tr>
<td>52</td>
<td>0.106</td>
</tr>
<tr>
<td>65</td>
<td>0.119</td>
</tr>
<tr>
<td>79</td>
<td>0.141</td>
</tr>
</tbody>
</table>

TABLE VII
DATA FOR THE CALIBRATION CURVE OF MERCURY DETERMINED BY THE DIRECT INJECTION METHOD
TABLE VIII

PRECISION OF THE ½ cc (1½ ng) MERCURY INJECTION

<table>
<thead>
<tr>
<th>Run number</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.119</td>
</tr>
<tr>
<td>2</td>
<td>0.115</td>
</tr>
<tr>
<td>3</td>
<td>0.125</td>
</tr>
<tr>
<td>4</td>
<td>0.108</td>
</tr>
<tr>
<td>5</td>
<td>0.128</td>
</tr>
<tr>
<td>6</td>
<td>0.119</td>
</tr>
</tbody>
</table>

Average = 0.119
σ = 0.007
**TABLE IX**

CALIBRATION DATA FOR MERCURY DETERMINED BY THE DIRECT INJECTION METHOD

<table>
<thead>
<tr>
<th>Gas composition</th>
<th>Cell temperature (°C)</th>
<th>Absorbance</th>
<th>Concentration of mercury in the cell at any one time (ng)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure argon</td>
<td>30</td>
<td>0.123</td>
<td>66</td>
</tr>
<tr>
<td>50% Argon - 50% Nitrogen</td>
<td>30</td>
<td>0.124</td>
<td>67</td>
</tr>
<tr>
<td>50% Argon - 50% Carbon monoxide</td>
<td>30</td>
<td>0.123</td>
<td>66</td>
</tr>
<tr>
<td>Pure nitrogen</td>
<td>30</td>
<td>0.124</td>
<td>67</td>
</tr>
<tr>
<td>Pure carbon monoxide</td>
<td>30</td>
<td>0.126</td>
<td>68</td>
</tr>
</tbody>
</table>

Average = 67 ng

\[ \sigma = 1.1 \]
Figure 16. Mercury Fluorescence Radiance Versus Nitrogen Concentration in Argon at Various Temperatures.
TABLE X

EFFECT OF INCREASING NITROGEN CONCENTRATION ON THE MERCURY FLUORESCENCE RADIANCE IN ARGON AT VARIOUS CELL TEMPERATURES

<table>
<thead>
<tr>
<th>% Nitrogen in argon</th>
<th>If (arbitrary units)</th>
<th>Cell temperature (30°C)</th>
<th>Cell temperature (726°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
<td></td>
<td>40</td>
</tr>
<tr>
<td>1</td>
<td>90</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>3</td>
<td>66</td>
<td>33</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>50</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>38</td>
<td>29</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>22</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>22</td>
<td>21</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>30</td>
<td>13</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>50</td>
<td>10</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>9</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>12</td>
<td>34</td>
<td></td>
</tr>
</tbody>
</table>
Figure 17. Plot of $1/Q$ Versus Nitrogen Concentration in Argon for Mercury at $30^\circ C$. 
<table>
<thead>
<tr>
<th>% Nitrogen in argon</th>
<th>$1/Q^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.11</td>
</tr>
<tr>
<td>3</td>
<td>0.15</td>
</tr>
<tr>
<td>5</td>
<td>0.20</td>
</tr>
<tr>
<td>3</td>
<td>0.27</td>
</tr>
</tbody>
</table>

$* \ 1/Q = \frac{I_f \ (\text{in pure argon})}{I_f \ (\text{in argon-nitrogen mixtures})}$
less pronounced as seen from the slope of the curve in fig. 16, which becomes assymptotic, the fluorescence radiance not decreasing below 8 arbitrary units. However when pure nitrogen is passed through the cell at 200 cc/min. with no argon present, the fluorescence radiance attains a value of 12 arbitrary units, a little higher than for the 50\% argon-50\% nitrogen mixture.

The above observed decrease in fluorescence radiance upon addition of increasing quantities of nitrogen is attributed primarily to the increase in quenching due to the increase in the concentration (or partial pressure) of nitrogen [nitrogen has a larger quenching cross-section for mercury than argon (82-84)].

The same effect was found for the addition of carbon monoxide to argon as seen in fig. 18 (table XII). In this case, however, the decrease in fluorescence radiance with increasing carbon monoxide concentration is more pronounced as seen from the slope of fig. 18. At 3\% of carbon monoxide in argon, the signal is already quenched to 2 arbitrary units (a quenching of 98 units relative to the signal in pure argon), this is due to the higher quenching efficiency, i.e., larger quenching cross-section for mercury of carbon monoxide as compared to nitrogen (82-84).

d. Temperature studies

(1) Effect of increase in cell temperature on the fluorescence signal in pure argon

Fig. 19 (table XIII) shows the variation of the fluorescence radiance as the cell temperature is increased from 30\°C to 805\°C. As one can observe, there is a steep decrease in the radiance from 30\°C to around 350\°C; above 350\°C the decrease is less
Figure 18. Mercury Fluorescence Radiance Versus Carbon Monoxide Concentration in Argon at Various Temperatures.
### TABLE XII

**EFFECT OF INCREASING CARBON MONOXIDE CONCENTRATION ON THE MERCURY FLUORESCENCE RADIANCE IN ARGON AT VARIOUS CELL TEMPERATURES**

<table>
<thead>
<tr>
<th>% Carbon monoxide in argon</th>
<th>$I_f$ (arbitrary units)</th>
<th>Cell temperature ($30^\circ C$)</th>
<th>Cell temperature ($726^\circ C$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
<td>39</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>50</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>20</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>2</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>0</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>
Figure 19. Mercury Fluorescence Radiance Versus Cell Temperature in Pure Argon.
TABLE XIII

EFFECT OF INCREASING CELL TEMPERATURE ON THE FLUORESCENCE RADIANCE OF MERCURY IN PURE ARGON

<table>
<thead>
<tr>
<th>Cell temperature (°C)</th>
<th>$I_F$ (arbitrary units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>100</td>
</tr>
<tr>
<td>150</td>
<td>70</td>
</tr>
<tr>
<td>390</td>
<td>49</td>
</tr>
<tr>
<td>726</td>
<td>39</td>
</tr>
<tr>
<td>775</td>
<td>38</td>
</tr>
<tr>
<td>850</td>
<td>37</td>
</tr>
</tbody>
</table>
pronounced and the curve becomes asymptotic, the radiance not falling below about $1/4$ units.

At first one is tempted to attribute this decrease in fluorescence radiance with increased temperature, to the fact that collision frequencies between mercury atoms and argon increase as temperature is increased, however a check of the absorbance signal as function of cell temperature showed a parallel decrease in absorbance as the cell temperature is increased from $30^\circ\text{C}$ to $80^\circ\text{C}$ as shown in fig. 2C (table XIV).

This same effect was observed by Robinson, et. al (80), using the same light source as the one utilized here and a long path absorption cell.

Since the concentration of mercury passing through the cell was previously found to be constant and independent of cell temperature (table VI), the above results are quite unusual and perplexing at first sight, since one knows that atomic absorption is not a function of temperature (96). Moreover we also know that at higher temperatures Doppler broadening of the absorption line would be expected, resulting in a greater overlap between absorption line and the center of the emitted line from the source thus increasing the absorption. Another factor governing total absorption, the oscillator strength, does not predict such a decrease in absorption with increased temperature.

One possible explanation of the above mentioned effect is to assume the line profile of the emission source to be highly self-reversed at the center as shown schematically in fig. 21. This was experimentally found by Robinson (80) and others (92, 93). The
Figure 20. Absorbance Versus Cell Temperature for Mercury in Pure Argon.
<table>
<thead>
<tr>
<th>Cell temperature (°C)</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>0.125</td>
</tr>
<tr>
<td>300</td>
<td>0.067</td>
</tr>
<tr>
<td>805</td>
<td>0.046</td>
</tr>
</tbody>
</table>
Figure 21. Schematic Diagram Illustrating the Effect of Increase in Cell Temperature on the Absorption Line Profile.
absorption signal is then primarily determined by the amount of overlap between the wings of the absorption line and the wings of the emission line since the center of the emission line is quite weak. The wings of the absorption line are primarily determined by the Lorentz broadening effect ($\gamma$), the half intensity width of which is inversely proportional to the square root of temperature at constant pressure ($\gamma \propto \sqrt{T}$). Therefore, as seen in fig. 31, when the cell temperature increases there is less overlap between the wings of the absorption line and those of the emitting line, since the absorption line width decreases at the wings with increased temperature. This decrease in overlap between the emission and absorption line, decreases the absorption signal. The decrease of the fluorescence radiance follows.

Another possible explanation of the decrease in the intensity of the absorption and fluorescence signals is given below. Assuming ideal behavior of the gas in the cell, it is easily seen from the equation of state ($pv = nRT$), that an increase in cell temperature ($T$) will cause a decrease in the number of atoms ($n$) present in the light path at any one time. The decrease in the number of atoms present in the cell causes a decrease in the intensity of the absorption and fluorescence signals.

(2) Effect of increase in cell temperature on the fluorescence signal in argon-nitrogen and argon-carbon monoxide mixtures

Figs. 16 and 18 (tables X and XII) show the effect of adding various amounts of nitrogen or carbon monoxide on the fluorescence radiance in argon at cell temperature $726^\circ$C. As for
the experiments at 30°C, a decrease in fluorescence radiance is observed upon increasing the nitrogen or carbon monoxide concentration. The decrease here, however, is not as pronounced as for the experiments at 30°C, especially as seen in fig. 17 for carbon monoxide.

Once again as seen from fig. 16, the fluorescence radiance in pure nitrogen atmosphere at 726°C is higher than the values for all the argon-nitrogen mixtures.

The percentage decrease in fluorescence radiance as a function of temperature for 3% nitrogen in argon and 3% carbon monoxide in argon is shown in fig. 22 (table XV). It is clear that upon increasing the cell temperature from 30°C to 726°C there is a gradual decrease in the quenching efficiency of nitrogen and carbon monoxide, relative to argon.

To illustrate the above statements: a 3% mixture of carbon monoxide in argon decreased the fluorescence radiance by 98 units at 30°C, while the same amount decreased it by only 35 units at 726°C. A 3% mixture of nitrogen in argon decreased the fluorescence radiance by 34 units, while the same amount decreased it by only 17 units at 726°C.

Fig. 23 (table XVI) shows the quenching effect of pure nitrogen, pure carbon monoxide and air relative to pure argon when the cell temperature was 850°C. The experimental conditions were slightly altered here in order to observe a fluorescence signal in pure carbon monoxide. It was necessary to increase the voltage on the detector and the amplifier gain. Even under these conditions purified tank air did not give a measurable fluorescence signal. The above results are in good agreement with the values given by Winefordner for the
Figure 22. Percentage Decrease of the Fluorescence Radiance of Mercury in 3% Nitrogen and 3% Carbon Monoxide in Argon at Various Cell Temperatures.
TABLE XV

PERCENTAGE DECREASE OF THE FLUORESCENCE RADIANCE OF MERCURY AS A FUNCTION OF CELL TEMPERATURE FOR THE 3% NITROGEN-ARGON AND THE 3% CARBON MONOXIDE-ARGON MIXTURES

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$I_F$ (pure argon)</th>
<th>$I_F$ (3% nitrogen-argon mixture)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>34</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>390</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td>726</td>
<td>17</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>$I_F$ (pure argon)</th>
<th>$I_F$ (3% carbon monoxide-argon mixture)</th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td>98</td>
<td></td>
</tr>
<tr>
<td>150</td>
<td>76</td>
<td></td>
</tr>
<tr>
<td>390</td>
<td>52</td>
<td></td>
</tr>
<tr>
<td>726</td>
<td>35</td>
<td></td>
</tr>
</tbody>
</table>
Figure 2. Mercury Fluorescence Radiance in Various Pure Gases at 850°C.
TABLE XVI

MERCURY FLUORESCENCE RADIANCE IN VARIOUS PURE GASES AT 850°C

Detector high voltage: 700 V, Amplifier gain: 10, Slit width: 300 μ, Gas flow rate: 200 cc/min.

<table>
<thead>
<tr>
<th>Gas</th>
<th>$I_f$ (arbitrary units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon</td>
<td>100</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>80</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>5</td>
</tr>
<tr>
<td>Air (from compressed air tank)</td>
<td>0</td>
</tr>
</tbody>
</table>
platinum-loop atomizer system (46) and for the values of the quenching
cross-section for mercury by argon, nitrogen, carbon monoxide and
oxygen (34).

e. Effect of increasing the mercury concentration on the
quenching of the fluorescence signal

In order to verify if any appreciable amount of self-
absorption was taking place in the cell, the mercury reservoir tem-
perature was increased from 4.5°C to 20°C. The quantity of mercury
entering the cell was now appreciably higher than in the previous
experiments. The fluorescence radiance in pure argon increased which
is to be expected from equation (2) and it was necessary to cut down
the amplifier gain in order to reset the signal at 100 arbitrary
units. When increasing amounts of nitrogen were mixed with the
argon, about the same relative amount of signal decrease was observed
(fig. 24, table XVII) as when the mercury pool temperature was at
4.5°C (see fig. 16, table X), thus indicating that self-absorption
was not appreciable in the fluorescence cell. Moreover the above
results indicate that the quenching efficiency of nitrogen relative
to argon is independent of the mercury concentration over the mercury
concentration range studied.

2. System with radio frequency heating

The results reported below are those for the system loaded
with the carbon rods which were heated by induction with the radio
frequency field. Pure argon at a flow rate of 200 cc/min. was passed
over the mercury pool maintained at 4.5°C as in the previously de-
scribed set up, and into the fluorescence cell. The fluorescence
signal was adjusted to 100 arbitrary units (conditions described
Figure 2h. Mercury Fluorescence Radiance Versus Nitrogen Concentration in Argon (Mercury Reservoir at 20°C).
### TABLE XVII

**EFFECT OF INCREASING NITROGEN CONCENTRATION ON THE MERCURY FLUORESCENCE RADIANCE IN PURE ARGON**

Mercury reservoir temperature: 20°C, Cell temperature: 30°C,
Detector high voltage: 650 V, Amplifier gain: 8, Slit width: 300 μ

<table>
<thead>
<tr>
<th>% Nitrogen in argon</th>
<th>$I_F$ (arbitrary units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
</tr>
<tr>
<td>1</td>
<td>90</td>
</tr>
<tr>
<td>2</td>
<td>75</td>
</tr>
<tr>
<td>3</td>
<td>68</td>
</tr>
<tr>
<td>5</td>
<td>55</td>
</tr>
<tr>
<td>8</td>
<td>41</td>
</tr>
<tr>
<td>22</td>
<td>22</td>
</tr>
<tr>
<td>50</td>
<td>12</td>
</tr>
</tbody>
</table>
earlier) and the argon flow was switched off. The side stem of the cell was then loaded with the carbon rods as described previously and air from the compressed air tank which was passed over activated charcoal to remove any metallic impurities was allowed to flow at 100 cc/min. over the mercury pool and into the cell. The radio frequency power was turned on and allowed to heat the carbon rods to about 1200°C as indicated by the optical pyrometer, although an absorption signal was observed, no fluorescence was detectable under the present conditions, even when the cell temperature was around 100°C. The air flow was switched off and purified argon was passed over the mercury pool reservoir and into the cell, the fluorescence signal started now to increase and attained a maximum value of 100 units when the cell temperature was about 450°C and the carbon rods were heated to about 1200°C. Nearly the same value of the fluorescence signal was attained in the previously described modified system without radio frequency heating of the cell to a temperature of 726°C (see table XIII). The fluorescence signal, in pure argon and under hot cell conditions described above, was then set to 100 arbitrary units by increasing the high voltage on the detector to 700 V, and the gain on the amplifier to 10. The argon flow was then switched off and purified air from the compressed air tank was passed over the mercury pool and into the cell at a flow rate of 100 cc/min. A fluorescence signal of 12 arbitrary units was now observed. Lowering the cell temperature or the carbon rods temperature did not appreciably change the intensity of the signal, even when the cell temperature was lowered to 200°C.

It is to be recalled here that in the previously described
modified system and under the same experimental conditions, the fluorescence signal obtained for pure carbon monoxide was 5 units, and for pure nitrogen was 80 units (see table XVI, fig. 23).

The absorption signal as mentioned earlier, was also monitored and found to behave in the same manner as described for the modified system without radio frequency heating, that is at high cell temperature, a decrease in absorption was observed.

It was not possible, using the same equipment described above, to increase further the gain on the amplifier or the high voltage on the detector since at higher voltage or gain conditions the noise level increased appreciably and the signal to noise ratio decreased accordingly.

In order to test the ability of the technique to atomize mercury, few crystals of mercuric chloride in a porcelain boat were introduced into the solid injector described previously, the mercury pool was disconnected. Air from the compressed air tank was passed at a flow rate of 200 cc/min. over activated charcoal, into the solid injector, over the carbon rods and into the fluorescence cell. The solid injector was heated at 200°C and the cell was maintained at 800°C. The radio frequency power was then turned on and a strong absorption signal was observed at 2537Å, thus indicating that free mercury metal was being introduced into the cell. No absorption was found at the adjoining 2528Å non-absorbing mercury line, thus confirming that the absorption at 2537Å was solely due to mercury atoms. The intensity of the fluorescence signal however was only 13 arbitrary units, thus demonstrating once again that although a large number of free mercury atoms were present in the cell as indicated by
the strong absorption signal, a large number of atoms in the excited state were returning to the ground state via a non-radiative deactivation process, i.e., quenching collisions with carbon monoxide and nitrogen molecules present in the cell.

B. CADMIUM STUDIES

1. Modified system without radio frequency heating

The results reported below are those for the simple system described earlier in which no carbon rods or radio frequency heating was used. Purified argon was passed in the cadmium injection system described earlier at 200 cc/min. and into the fluorescence cell. The signal was adjusted to 100 arbitrary units, various amounts of purified nitrogen were then introduced into the cell and the fluorescence signal recorded, the same was done with carbon monoxide.

a. Stability of the fluorescence and absorption signals

Fig. 25 shows a plot of $I_f$ (fluorescence radiance in arbitrary units) versus time for the cadmium $\text{2288A}$ in pure argon atmosphere at cell temperature $355^\circ C$. The noise level was 3 arbitrary units (noise level $3\%$).

Fig. 26 (table XVIII) shows a plot of absorbance versus time for the $\text{2288A}$ cadmium line in pure argon at cell temperature $355^\circ C$. The absorption signal was found to be the same for pure nitrogen and pure carbon monoxide and also for various mixtures of argon with these two gases.

Since the cadmium Osram lamp was found to be stable (fig. 10) the above results indicate that a fairly constant amount of cadmium was being introduced into the cell over long periods of time.
Figure 25. Fluorescence Radiance Versus Time for the 2288Å Line of Cadmium in Pure Argon at 355°C.
Figure 26. Absorbance Versus Time for Cadmium in Pure Argon at 355°C.
<table>
<thead>
<tr>
<th>Time (min.)</th>
<th>Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>0.523</td>
</tr>
<tr>
<td>20</td>
<td>0.509</td>
</tr>
<tr>
<td>30</td>
<td>0.516</td>
</tr>
<tr>
<td>40</td>
<td>0.523</td>
</tr>
<tr>
<td>50</td>
<td>0.530</td>
</tr>
<tr>
<td>60</td>
<td>0.523</td>
</tr>
</tbody>
</table>
b. Calibration method

In order to have an idea of the amount of cadmium introduced into the cell; the exhausted gases from the cell were collected in BOD bottles equipped with glass fritted bubblers and glass beads and containing a 1 N solution of nitric acid in deionized-distilled water. The cadmium solutions were analyzed by a model 403 Perkin-Elmer Atomic Absorption instrument, after collection periods ranging from 1 to 1 hr.

(1) Standard cadmium solutions

Standard cadmium solutions were prepared in the range of 0.1 to 1.0 µg/ml from a 1000 ppm stock solution made from reagent grade cadmium nitrate dissolved in concentrated nitric acid and diluted with distilled water to a final concentration of 1 N in nitric acid.

(2) Experimental conditions of the analysis

Hollow cathode current: 1 mA
Air-acetylene flame
Wavelength: 2288 Å
Slit width: 7 Å

(3) Calibration curve

The calibration curve for the range 0.1 to 0.7 µg/ml is shown in fig. 27 (table XIX). Table XX shows the data and results for the analysis of three collected samples, the average cadmium concentration found at any time in the cell was 0.014 µg (14 ng). This figure was arrived at by taking into account the volume of the cell which was 20.3 ml.
Figure 27. Calibration Curve for Cadmium Determined by the Perkin-Elmer Atomic Absorption Instrument.
TABLE XIX
DATA FOR THE CALIBRATION CURVE OF CADMIUM DETERMINED BY THE PERKIN-ELMER ATOMIC ABSORPTION INSTRUMENT

<table>
<thead>
<tr>
<th>Cadmium concentration (µg/ml)</th>
<th>Absorbance (average of 10 values)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>0.011</td>
</tr>
<tr>
<td>0.2</td>
<td>0.020</td>
</tr>
<tr>
<td>0.4</td>
<td>0.041</td>
</tr>
<tr>
<td>0.6</td>
<td>0.062</td>
</tr>
<tr>
<td>0.8</td>
<td>0.084</td>
</tr>
</tbody>
</table>
TABLE XX

CALIBRATION DATA FOR CADMIUM DETERMINED BY THE PERKIN-ELMER ATOMIC ABSORPTION INSTRUMENT

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Sample collection time (min.)</th>
<th>Final volume of collecting solution (ml)</th>
<th>Absorbance (average of 10 values)</th>
<th>Cadmium concentration at any one time in the cell (µg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>960</td>
<td>25.0</td>
<td>0.055</td>
<td>0.014</td>
</tr>
<tr>
<td>2</td>
<td>840</td>
<td>24.0</td>
<td>0.049</td>
<td>0.014</td>
</tr>
<tr>
<td>3</td>
<td>1085</td>
<td>24.0</td>
<td>0.068</td>
<td>0.016</td>
</tr>
</tbody>
</table>
c. **Effect of increasing nitrogen and carbon monoxide concentrations on the cadmium fluorescence signal in argon at 355°C**

The same effect observed previously for mercury was seen again here. At low nitrogen concentrations (up to 8%), there is a rapid decrease in signal as shown in fig. 28 (table XXI). At higher nitrogen concentrations the decrease is less pronounced as shown in fig. 29 (table XXII). Contrary to the results for mercury, the fluorescence radiance in pure nitrogen did not have a higher value than for the argon-nitrogen mixtures.

The same effect was also found for the addition of carbon monoxide to argon as seen in fig. 30 (table XXIII). The decrease in fluorescence radiance with increasing carbon monoxide concentration is more pronounced, however it is not as strong as for mercury, since a signal could still be detected at 80% carbon monoxide in argon. No signal could be detected in pure carbon monoxide.

It is interesting to note here that the 3261Å cadmium resonance fluorescence signal (which was weak in argon compared to the 2288Å line) increased instead of decreasing upon addition of low amounts of nitrogen (up to 14%), higher concentration of nitrogen caused a decrease in the fluorescence radiance as seen in fig. 31 (table XIV). This same effect was observed by West and Alder (51) and by Krysmanski (96). No further quantitative studies of the 3261Å line were undertaken since the fluorescence radiance at this wavelength was relatively weak.
Figure 25. Plot of $1/Q$ Versus Nitrogen Concentration in Argon for Cadmium at 700 °C.
TABLE XXI

EFFECT OF LOW NITROGEN CONCENTRATION ON THE CADMIUM FLUORESCENCE RADIANCE AT 2288Å IN ARGON AT 355°C

<table>
<thead>
<tr>
<th>% Nitrogen in argon</th>
<th>1/Q*</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>0.14</td>
</tr>
<tr>
<td>5</td>
<td>0.16</td>
</tr>
<tr>
<td>8</td>
<td>0.22</td>
</tr>
</tbody>
</table>

* $\frac{1}{Q}$ = \frac{If \ (in \ pure \ argon)}{If \ (in \ argon-nitrogen \ mixtures)}
Figure 29. Cadmium Fluorescence Radiance at 2288 Å Versus Nitrogen Concentration in Argon at Various Temperatures.
<table>
<thead>
<tr>
<th>% Nitrogen in argon</th>
<th>( I_f ) (arbitrary units)</th>
<th>( \text{Cell temperature} \ (355^\circ \text{C}) )</th>
<th>( \text{Cell temperature} \ (810^\circ \text{C}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>73</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>61</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>45</td>
<td>44</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>35</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>30</td>
<td>36</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>15</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>8</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>6</td>
<td>21</td>
<td></td>
</tr>
</tbody>
</table>
Figure 30. Cadmium Fluorescence Radiance at $2238\AA$ Versus Carbon Monoxide Concentration in Argon at Various Temperatures.

Cell temperature 355°C

Cell temperature 550°C

Carbon monoxide

[Graph showing fluorescence radiance versus carbon monoxide concentration at different cell temperatures.]
TABLE XXIII
EFFECT OF INCREASING CARBON MONOXIDE CONCENTRATION ON THE CADMIUM FLUORESCENCE RADIANCE AT 2288 Å IN ARGON AT VARIOUS CELL TEMPERATURES

<table>
<thead>
<tr>
<th>% Carbon monoxide in argon</th>
<th>$I_f$ (arbitrary units)</th>
<th>Cell temperature (355°C)</th>
<th>Cell temperature (810°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>100</td>
<td>60</td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>79</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>68</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>45</td>
<td>46</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>25</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>11</td>
<td>32</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>7</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>6</td>
<td>14</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>3</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>
Figure 31. Cadmium Fluorescence Radiance at 3261 Å Versus Nitrogen Concentration in Argon at 355°C.
<table>
<thead>
<tr>
<th>% Nitrogen in argon</th>
<th>$I_f$ (arbitrary units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>20</td>
</tr>
<tr>
<td>3</td>
<td>39</td>
</tr>
<tr>
<td>5</td>
<td>45</td>
</tr>
<tr>
<td>8</td>
<td>49</td>
</tr>
<tr>
<td>14</td>
<td>50</td>
</tr>
<tr>
<td>50</td>
<td>25</td>
</tr>
<tr>
<td>80</td>
<td>7</td>
</tr>
<tr>
<td>100</td>
<td>5</td>
</tr>
</tbody>
</table>
d. Temperature studies

(1) Effect of increase in cell temperature on the fluorescence signal in pure argon

Upon increasing the cell temperature from 355°C to 850°C, the fluorescence signal decreased by 40 units and stabilized at 60 units since no further decrease was noticed upon increasing the temperature above 850°C. The absorption signal was also monitored and found to decrease slightly with increased temperature. This is similar to the effect previously observed for mercury, and the same explanation could be given here since the Osram lamp is well known to have a broad self-reversed line profile at 2288 Å (92).

(2) Effect of increase in cell temperature on the fluorescence signal in argon-nitrogen and argon-carbon monoxide mixtures

Figs. 29 and 30 (tables XXII and XXIII) show the effect of adding various amounts of nitrogen or carbon monoxide on the fluorescence radiance in argon at cell temperature 850°C. As for the experiments at 355°C, a decrease in fluorescence radiance is observed upon increasing the nitrogen or carbon monoxide concentration. The decrease, however, is less pronounced than for the experiments at 355°C, indicating a decrease in fluorescence quenching cross-section with increase in temperature. No signal was observed for pure carbon monoxide at 850°C.

Fig. 32 (table XV) shows the quenching effect of pure nitrogen, pure carbon monoxide and air relative to pure argon when the cell temperature was maintained at 850°C. It was necessary to alter the experimental conditions here in order to observe a signal for carbon monoxide. However, even under these conditions air did not give a
Figure 32. Cadmium Fluorescence Radiance in Various Pure Gases at 850°C.
**TABLE XXV**

**CADMIUM FLUORESCENCE RADIANCE IN VARIOUS PURE GASES AT 850°C**

Detector high voltage: 800 V, Amplifier gain: 11, Slit width: 300 μ, Gas flow rate: 200 cc/min.

<table>
<thead>
<tr>
<th>Gas</th>
<th>$I_f$ (arbitrary units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Argon</td>
<td>100</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>33</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>1</td>
</tr>
<tr>
<td>Air (from compressed air tank)</td>
<td>0</td>
</tr>
</tbody>
</table>
measurable signal.

The above results parallel those for mercury and agree rather well for the relative values given by Winefordner (17) and West (15) for the cadmium fluorescence radiance in argon, nitrogen, carbon monoxide and air.

System with radio frequency heating

The results reported below are those for the system loaded with the carbon rods which were heated by induction with the radio frequency field. Pure argon at a flow rate of 200 cc/min. was passed over the cadmium injector maintained at 550°C as in the previously described set up, and into the fluorescence cell maintained at 850°C. The fluorescence signal was adjusted to 100 arbitrary units (conditions described earlier) and the argon was switched off. The side stem of the cell was then loaded with the carbon rods as described previously and air from the compressed tank which was passed over activated charcoal was allowed to flow at 200 cc/min. over the cadmium injector and into the cell. The radio frequency power was turned on and allowed to heat the carbon rods to about 1200°C as indicated by the optical pyrometer, although an absorption signal was observed, no fluorescence was detectable under the present conditions. The air flow was switched off and purified argon was passed over the cadmium injector and into the cell maintained at 850°C, the fluorescence signal started to increase now and attained a maximum value of 100 units. Nearly the same value of the fluorescence signal was attained in the previously described modified system without radio frequency heating of the cell to a temperature of 850°C (see table XXII).

The fluorescence signal, in pure argon and under hot cell
conditions described above, was then set to 100 arbitrary units by increasing the high voltage on the detector to 150 V, and the gain on the amplifier to 11. The argon flow was then switched off and purified air from the compressed air tank was passed over the cadmium injector and into the cell at a flow rate of 200 cc/min. A weak fluorescence signal of 1 arbitrary units was now observed. Lowering the cell temperature or the carbon rods temperature did not appreciably change the intensity of the signal. It is to be recalled here that in the previously described modified system and under the same experimental conditions, the fluorescence signal obtained for pure carbon monoxide was 1 unit, and for pure nitrogen was 1.5 units (see table XV, fig. 2c).

It was not possible, using the same equipment described earlier, to increase further the gain on the amplifier or the high-voltage on the detector since at higher voltage and gain conditions the noise level increased appreciably and the signal to noise ratio decreased accordingly.

In order to test the ability of the technique to atomize cadmium, a few crystals of cadmium chloride in a porcelain boat were introduced into the solid injector described previously. Air from the compressed air tank was passed at a flow rate of 200 cc/min. over activated charcoal, into the solid injector, over the carbon rods and into the fluorescence cell. The solid injector was heated at 700°C and the cell maintained at 850°C. The radio frequency power was then turned on and a strong absorption signal was observed at 2283Å, thus indicating that free cadmium metal was being introduced into the cell. No absorption was found at the adjoining 2264Å non-absorbing cadmium
line, thus confirming that the absorption at 2283Å was solely due to cadmium atoms. The fluorescence signal, however was not detectable, thus demonstrating once again that although a large number of free cadmium atoms were present in the cell as indicated by the strong absorption signal, a large number of atoms in the excited state were returning to the ground state via a nonradiative deactivation process, i.e., quenching collisions with carbon monoxide and nitrogen molecules present in the cell.
DISCUSSION

Since first noticed by Wood (97, 98) for mercury, quenching of the resonance fluorescence radiation was investigated for other elements such as cadmium (91, 96), mercury (82-84) and the alkali metals (89). These experiments indicated that quenching is a general phenomenon that takes place whenever collisions of the second kind between foreign gas molecules and excited atoms lead to the removal of the latter from the excited state before they have time to radiate. "Quenching" (Q) is defined as (99):

\[
Q = \frac{\text{Intensity of fluorescence radiation with foreign gas}}{\text{Intensity of fluorescence radiation without foreign gas}} \quad (6)
\]

If the following conditions are fulfilled:

a) The absorbing atoms in the fluorescence cell are at such a low concentration that only primary resonance radiation is emitted which is not further absorbed on its way out.

b) The pressure of the foreign gas is low so that Lorentz broadening is negligible.

Q is then given by the Stern-Volmer equation (99).

\[
Q = \frac{1}{1 + \tau Z_Q} \quad (7)
\]

where \( \tau \) is the lifetime of the excited atom and \( Z_Q \) is the number of quenching collisions per sec. per cc, per excited atom.

\( Z_Q \) can be calculated on the basis of a Maxwellian distribution of velocities resulting in the expression (91):

\[
Z_Q = 2 \pi n_0 c Q^2 [2 \pi RT (1/M_1 + 1/M_2)]^{\frac{3}{2}}
\]

where \( M_1 \) and \( M_2 \) are the molecular weights of the colliding particles.
N and n their molecular concentrations and R the universal gas constant.

If R is expressed in the form of the pressure in mm of Hg, \( \frac{1}{\Omega} \), the "effective" quenching cross-section is given by:

\[
\sigma_Q^2 = \frac{1/(Q.p)}{\tau \times \exp \left[ \frac{\Delta N/RT \left( 1/M_1 + 1/M_2 \right)\}^2}{\left( \frac{1}{M_1} + 1/M_2 \right)} \right]}
\]

In practice one measures \( Q \) as function of \( p \), the pressure of the foreign gas. \( 1/Q \) is plotted versus \( p \), the slope of the resulting straight line (see figs. 16 and 23) is the numerator of the above equation, the denominator is easily calculated from known values of \( \tau \) and thus values of \( \sigma_Q^2 \) are obtained.

Table XVI shows \( \sigma_Q^2 \) values for the \( \text{H}_\beta \) mercury line and the cadmium \( \text{H}_\beta \) line in nitrogen and carbon monoxide. No data are available in the literature for the cadmium \( \text{H}_\beta \) line, at present.

The values in table XVI indicate:

a) that the quenching efficiency of carbon monoxide is higher than that of nitrogen for both elements, since \( \sigma_Q^2 \) for mercury and \( \sigma_Q^2 \) for cadmium.

b) that the quenching efficiency of oxygen for mercury is about eighty times higher than that of nitrogen for the same element.

The higher \( \sigma_Q^2 \) value for carbon monoxide over nitrogen is due to the fact that it quenches mercury \( (3P_1) \) excited atoms mainly to the ground state \( (3S_0) \), while nitrogen quenches the \( 3P_1 \) excited mercury atoms mainly to the metastable states \( (3P_0, 3P_2) \). The above data agree quite well with the results reported earlier since we also observed stronger quenching effects due to
TABLE XXVI
EFFECTIVE QUENCHING CROSS-SECTIONS FOR MERCURY AND CADMIUM

<table>
<thead>
<tr>
<th>Gas</th>
<th>$\sigma_0^2$ ($\text{Å}^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mercury (2537\text{Å} line)</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.73 (84), 0.60 (59)</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>21.7 (84), 20.4 (82)</td>
</tr>
<tr>
<td>Oxygen</td>
<td>60.5 (84), 62.8 (82)</td>
</tr>
<tr>
<td></td>
<td>Cadmium (3261\text{Å} line)</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.022 (81)</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>0.15 (81)</td>
</tr>
</tbody>
</table>


carbon monoxide over nitrogen for the two elements studied. (See results under modified systems.)

The decrease in quenching cross-sections with increase in temperature or relative velocities of the colliding particles, as observed earlier, is reported by Hooymayers and Alkemade (10), by Hrycyszyn and Krause (10), by Jenkins (10) and by Gatzke (10) for the alkali metals. No such data are available in the literature at present for mercury and cadmium, but the same trend is to be expected mainly a decrease in quenching cross-sections, as temperature increases. No clear explanation is available at present concerning this effect although some authors attribute it to self-absorption (10) or to intermediate activated complex formation at low temperature (10, 10) or to resonance defect between the energy levels of the excited atom and the colliding molecule (10).

From all the above cited results, one fact stands out that is, the quenching cross-sections of nitrogen and carbon monoxide are much lower for flame cells (temperature ranging from 1400°K to 2200°K) than for experiments undertaken in non-flame cells (temperature ranging from 400°K - 900°K) (10).

In conclusion, our results for mercury and cadmium in the modified systems described earlier demonstrate quite well the quenching effect of nitrogen and carbon monoxide on the resonance fluorescence signals of these elements in a non-flame cell. They clearly explain the reason why a very weak fluorescence signal was obtained in the actual system with radio frequency heating, where carbon monoxide was produced in the atomizer and nitrogen was introduced with the air sample to be analyzed.
This is a clear-cut case where atomic absorption spectroscopy is superior to atomic fluorescence since the former method is not crippled by the quenching effect described above.

Moreover in view of the strong quenching efficiencies of oxygen and nitrogen for many elements, the future of atomic fluorescence as applied to the direct determination of air pollutants without prior concentration, i.e., by passing ambient air in a cell and measuring the atomic fluorescence signal of the elements to be determined, is very bleak indeed.
PART II

ANALYSIS OF AIRBORNE PARTICULATES BY X-RAY PHOTOELECTRON SPECTROSCOPY (E.S.C.A.)
INTRODUCTION

Airborne particulates are defined as "dispersed solid or liquid matter in a gaseous medium, in our case, air" (10¹⁻⁸). Particle size in the atmosphere ranges in diameter from 0.01 μ to about 10 μ (10⁻⁸). Very small particles (i.e., diameter below 1 x 10⁻⁶ μ) have very short lifetimes because they adhere rapidly to the larger particles, while very large particles (i.e., diameter above 10 μ) remain airborne only for short periods of time due to sedimentation and are thus restricted to the close vicinity of their source of emission.

Particulate matter of various descriptions loads our atmosphere. Nature furnishes part of the load in the form of bacteria, soil dust, spores, pollen, volcanic dust, meteoritic dust and sea salt. However since the turn of this century man's activities have tremendously increased the particulate loading of the atmosphere. Particulate emissions from stationary sources in the U.S. only, were estimated at 1.5 x 10⁷ tons/year (10⁷). The major stationary sources were: electric power generation plants, crushed stone industry, forest products industry, agricultural activities, cement industry and the iron and steel industries (10⁷). Thus in addition to the natural particles, which range in concentration from 5 to 10 μg/m³ (10⁻⁶), one finds fly ash and smoke from combustion processes, oxide fumes from metallurgical refining and many more other products of industrial activities such as those mentioned earlier, bringing the total atmospheric load to a range of 100 to 3000 μg/m³ and above, the upper limit being that for large heavily polluted urban centers and industrial agglomerations.
In the past decade a considerable amount of research has been carried out on the composition of airborne particulate matter. Methods such as X-ray diffraction and fluorescence, emission spectros­copy, neutron activation, mass spectrometry, atomic absorption and fluorescence spectroscopy, ring-oven techniques, polarography to cite only few, have been used with some amount of success (110-112).

The bulk of the work, however, has been mostly devoted to the determination of particle size and to the identification of the chemical elements present with minor efforts for the identification of actual chemical species or to the molecular forms of the various elements identified as present by elemental analysis. The need for the identification of the actual chemical compounds present in the airborne particulates stems from the well known fact that some elements are much more toxic in one chemical form than in another, i.e., mercury is very toxic as methyl mercury but not as toxic in the form of calomel, chromium is more toxic in the +6 oxidation state than in the +3 state. Therefore, it is imperative that in order to assess the potential health hazards and toxicity of certain air pollutants, their exact chemical form should be known. The above knowledge is also desirable in order to set reasonable safety standards for these pollutants in the atmosphere. Moreover by elucidating the exact chemical forms of air pollutants it will become easier to understand and interpret the different and complex chemical reactions taking place in the atmosphere.

Heretofore, chemical states of elements such as sulfur, nitrogen and phosphorous were determined by using specific colorimetric re­actions for the anions $SO_4^{2-}$, $NO_3^-$, $PO_4^{3-}$ and $NH_4^+$ (110-113). These
methods are time consuming and sample destructive. They usually involve sample collection with subsequent separation into its components followed by isolation and identification.

Recently other analytical methods, such as electron spin resonance spectroscopy (E.S.R.) and electron microscopy, were explored. E.S.R. was used to study the chemical forms of iron particulates collected at a site in the Netherlands (119). Electron microscopy was used to study the chemical forms of elements such as sulfur and nitrogen (117, 118) and lead (117) in the atmosphere.

In the following pages we will introduce a relatively new analytical technique namely X-ray photoelectron spectroscopy and show how it could be used to determine the actual chemical species present in airborne particulates with no prior sample treatment and in a non-destructive way.

A. HISTORICAL DEVELOPMENT OF PHOTOELECTRON SPECTROSCOPY

The history of photoelectricity began with the experiments of Heinrich Hertz on electrical resonance in 1887. Hertz discovered that ultraviolet light falling on certain metals caused them to emit negatively charged particles (113, 115). Stimulated by the investigations of Hertz, Hallawachs in 1888 made a more thorough investigation of the phenomenon (119). In the following year Elster and Geitel published a series of studies on the photoelectric phenomenon (120). They reported a photoelectric effect in alkali and other metals and constructed the first photoelectric cells.

P. Lenard and J.J. Thomson showed in 1899 that the electrically negative particles emitted under the influence of incident radiation were electrons (114, 121).
Lenard (122) also discovered that the kinetic energy with which the electrons are released is independent of the intensity of the light, the number of electrons emitted however is proportional to this intensity. This was one of the basic facts upon which Einstein built his photoelectric theory.

In 1905, Einstein (114) demonstrated that in the photoelectric effect the incident photon transmits its energy directly and completely to an orbital electron of the atom concerned. Part of the photon energy is consumed in supplying the binding energy of the orbital electron and any remainder is given to the electron as kinetic energy. Thus if \( E_b \) represents the binding energy of the electron, \( h \) Planck's constant and \( \nu \) the frequency of the incident photon, then the energy of this photon is \( h\nu \) and the kinetic energy \( E_k \) of the electron when ejected is equal to \( h\nu \) minus \( E_b \) \( (E_k = h\nu - E_b) \). Clearly the photon energy must be at least as large as the binding energy for a given shell before electrons in that shell can absorb such photons and be ejected.

After their discovery by Röntgen in 1896 (124, 125), it was realized by Perrin (126) in 1897 that X-rays have the power (as ultraviolet light) of ejecting high-speed electrons from the surface of materials on which they are incident.

A large amount of work was then carried out in order to determine the relation between the velocity of emission of photoelectrons and the wavelength of the incident light.

The investigations of Compton (125, 127, 128), Richardson (127), Hughes (117) and Millikan (129) proved conclusively that the maximum energy of emission of photoelectrons is a linear function of the
frequency of light. For a particular metal a certain minimum fre-
quency is necessary to produce any liberation of electrons at all.
As the frequency increases so does the energy of emission or the
positive potential required to prevent the emission. A remarkable
instance of extrapolation was afforded by the employment of the
formula deduced from experiments on ultraviolet light to calculate
the wavelength of X-rays, assuming this to behave in the same way as
ultraviolet light of extremely short wavelength. The value so cal-
culated by Barkla and Martyn was in good agreement with that obtained
from observations on the interference fringes produced by reflection
of the X-rays by a crystal of rock-salt [work of Bragg (124) on X-rays
diffraction]. The earliest successful attempts to measure the speed
of electrons emitted upon X-rays incidence on metallic surfaces were
made by Dorn in 1900 (150) and Innes in 1907 (131). The speed ap-
peared to be independent of the intensity of the rays in accordance
with Einstein's photoelectric equation.

Previous to 1910 the velocity and energy distribution of photo-
electrons ejected by X-rays from solid metal surfaces was studied by
the stopping potential method (Innes 1907) which was employed in
studying photoelectron velocities generated by ultraviolet light.
Due to the high voltages requirement this method was limited to soft
X-rays only.

The magnetic deflection method originally developed by Classen
(1908) was applied to the analysis of photoelectron velocities by
H.R. Robinson and Rawlinson in 1914 (132) and later used by deBroglie
and Whiddington (133, 131). The electrostatic analyzer was not in-
troduced until 1929 by Hughes, Rojansky and McMillen (134) and later
developed by Purcell in 1927 \( (139) \) and Herzog in 1940 \( (136) \).

The spectra were recorded on photographic plates in the early work, later the Geiger counter was used by Chadwick \( (1911) \). Watson and Van den Akker introduced the Geiger-Müller counter in 1931 \( (137) \). The electron distributions obtained by Robinson and deBroglie around 1930 \( (132, 133, 139) \) were characterized by long tails with edges at the high energy end. By measuring the positions of the edges it was possible to determine the energy of the photoelectrons ejected from the different atomic shells of the element under investigation. From the known energy of the X-ray lines in the primary X-ray beam, the binding energies of electrons in the different shells could be calculated, by applying Einstein's equation.

Another approach was to vary the X-ray wavelength, it was then possible to investigate the onset of ionization of deep-lying electronic shells. This technique was called absorption-edge spectroscopy. In 1920, J. Bergengren \( (123) \) discovered that the positions of X-ray absorption-edges depended on the types of bonding or valence states of the atoms of the material investigated.

In 1930, attempts were again made by Robinson and Young \( (140) \) to study chemical displacements in X-ray produced electron spectra. Progress, however, was hampered in this direction due to two main reasons: the line separations in X-ray emission spectra are generally very small and furthermore they are difficult to interpret theoretically. In X-ray absorption spectra, the separation between absorption edges are larger but on the other hand the effects are much more difficult to study because of the edge structures which are often further complicated by additional structures on the high energy sides.
After all the above-mentioned early investigations, the electron spectroscopic approach almost completely disappeared. The reason for this recession is that the results could not compete in accuracy with those obtained from other X-ray spectroscopies such as X-ray absorption and X-ray emission techniques. The edge positions of the electron distributions in the early work (i.e., Robinson and de Broglie) were not well defined, because of the energy absorption of the electrons emerging from the foil.

As reported by K. Siegbahn (141) a comparison of the observed binding energies from M. Siegbahn (1931) and A.E. Lindh (1930) showed considerably greater spread and greater uncertainty throughout. Steinhardt and co-workers (142, 143) in 1951, tried to extend the early works by developing an instrument capable of measuring X-ray photoelectron energies from 6 to 17.5 keV. The spectrometer was a 180° magnetic deflection electron energy selector. A Geiger-Müller counter was used as detector. Later in 1953 (144), the magnetic analyzer was replaced by a radial, inverse first-power, electrostatic field analyzer. An attempt was made to quantitatively analyze a silver-gold alloy and also to study the effect, on the photoelectrons, of a built-up film of barium stearate over gold. The spectral resolution of the instrument, however, was not high enough to yield a true line spectrum. Similar studies were also reported by Henke in 1962 (145), who is also responsible for improving the original design of the spherical electrostatic analyzer first used by Purcell in 1938 (146).

High-resolution photoelectron spectroscopy as we know it today is mainly due to the extensive research program undertaken by
K. Siegbahn and co-workers at the University of Uppsala in Sweden. In a 1946 publication K. Siegbahn and N. Svartholm \(^{147}\) presented the basic theory of a double focusing iron-free magnetic spectrometer for high resolution energy analysis by photo ejected electrons.

In 1954, the first instrument was built at Uppsala \(^{141}\) and a high resolution photoelectron spectrum produced by X-rays was recorded. The spectrum showed very sharp lines which could be resolved from the edge of each electron veil. The lines were found not to undergo any energy absorption and the sharp peaks were attributed to the binding energies of the relevant inner shells.

This technique was given the acronym of E.S.C.A. (electron spectroscopy for chemical analysis) by the Siegbahn group \(^{141}\), in order to distinguish it from other well-known photoelectron spectroscopies such as Auger electron spectroscopy and molecular photoelectron spectroscopy. Auger electrons are emitted when an electron from one of the inner shells is ejected from the atom, due to X-ray irradiation, the vacancy is then filled by an electron from an outer shell and the energy released is transferred to another outer electron which leaves the atom as an Auger electron. Contrary to E.S.C.A., the kinetic energy of an Auger electron is independent of the primary radiation and depends only on the energy levels of the electronic states involved.

In molecular photoelectron spectroscopy, also known as P.E.S. (photoelectron spectroscopy), the source is vacuum ultraviolet and the technique is mainly concerned with the ejection of electrons from valence orbitals of molecules \((E_b < 30 \text{ eV})\) in contrast to E.S.C.A. which is concerned with electrons ejected both from inner
and outer orbitals. Furthermore, E.S.C.A. can be applied to solid, vacuum and liquid samples while P.E.S. is mainly limited to gases, although information about solid state band structure can be obtained under conditions of high vacuum and with special precautions as to the surface conditions.

B. THEORY

Photoionization is the basic process for emission of electrons from atoms in the E.S.C.A. technique.

A quantum of radiation, $h\nu$, from the X-ray source falls on the atom and causes ejection of electrons from the different electronic orbitals. The electrons are ejected from the $1s$ (K shell), $2s$ (L1 shell), $2p$ (L2, L3 shells) etc., to the free electron level as illustrated in fig. 35. The free electron level is that energy level where the electron has become free of its normal atomic and molecular forces.

Photoionization thus leaves a hole in the atom and the nature of the hole states is indicated by the term symbols on the right side of fig. 35. For example the photoejection of a $1s$ electron leaves a $2s^\frac{1}{2}$ state or a K hole.

The energy, $E_{\text{X-ray}}$, of the incident X-ray photon during the photoejection of an electron from a solid sample is distributed among four processes as seen in fig. 34.

First $E_b$ the binding energy relative to the Fermi level of the material in which it is found.

Second $\Phi_s$ the work function of the material which is the energy needed to raise the electron from the Fermi level to the free electron level.
Figure 33. Primary Processes for Electron Photoejection from a Solid Electrical Insulator.
Figure 34. Energy Diagram of Sample and Photoelectron Spectrometer Material.
Third the recoil energy $E_r$ result of the principle of conservation of momentum in the photoejection process.

Fourth $E_k$ the kinetic energy of the electron in space after leaving the sample.

Conservation of energy in the photoelectric process thus requires the kinetic energy $E'_k$ of the photoejected electron to be given by the following equation:

$$E'_k = E_{x\text{-ray}} - E'_b - E_r$$  \hspace{1cm} (9)

($E'_k$ is the kinetic energy of the electron as it leaves the sample before entering the spectrometer.)

K. Siegbahn and co-workers (141) applying the law of conservation of momentum for the case when the recoil is in the direction of the incoming photon derived the following equation as the upper limit for $E_r$.

$$E_r = E_{x\text{-ray}} \frac{m}{M} \left[ \frac{E_{kin}}{E_{x\text{-ray}}} + \frac{(2E_{kin})^{\frac{1}{2}}}{mc^2} + \frac{E_{x\text{-ray}}}{mc^2} \right]$$  \hspace{1cm} (10)

$M$ and $m$ are the masses of the recoiling atom and the photoelectron respectively. They found that in most cases recoil energy is generally unimportant for electron ejection from light atoms. If Al Kα radiation is used, recoil energy is unimportant for atoms heavier than lithium and finally if CuKα is used as a source of X-ray radiation, recoil energy is unimportant in atoms heavier than sodium.

Due to the existence of a small electric field between the source and the spectrometer (even if both are grounded), the kinetic energy $E_k$ of the electron when it enters the spectrometer is slightly different from the energy $E'_k$ which it has on emerging from the sample.
The electric field exists because when source and spectrometer are grounded their Fermi levels are the same, thus any difference in work function of the source material and the spectrometer material gives a difference in macro-potential or contact potential $E_c$ resulting in an electric field between source and spectrometer.

If the Fermi level is chosen as reference level for determining binding energies ($E_b = 0$ at the Fermi level), conservation of energy requires:

$$E_b = E_{\text{X-ray}} - E_{\text{kin}} - \phi_{sp} \quad (11)$$

$\phi_{sp}$ is the work function of the spectrometer material and is assumed to be constant with time for a given spectrometer, thus it is possible to determine accurately relative binding energies. If absolute binding energies are to be measured an accurate determination of $\phi_{sp}$ is needed.

E.S.C.A. provides accurate determination of binding energies for almost all elements and for all the electronic levels from the K level to the Fermi level. Metals, semi-conductors and insulators may all be studied.

Tables of electron binding energies are available based on E.S.C.A. measurements (111).

It was realized early by Siegbahn and co-workers (111) that binding energies obtained from the E.S.C.A. spectrum are not a property solely of the atom but also of its chemical environment, i.e., of the molecular structure. A clear demonstration of this phenomenon not come, however, until 1964 when they observed two lines for sulfur in the $S_{1s}$ spectrum of sodium thiosulfate (148). Because of
the known structure of the sodium thiosulfate molecule the origin of the two lines observed for sulfur was attributed to the fact that the sulfur atoms are non-equivalent, one being in the $-2$ formal oxidation state and the other in the $+6$ state. The separation between the two S peaks is termed "chemical shift".

Chemical shifts have been compiled for many elements in different matrices: organic and inorganic (141, 142).

The shifts are due to the influence of the molecular charge distribution on the shielding of core electrons by valence electrons. Since core electrons are attracted by the nucleus and repulsed by outer or valence electrons, this repulsive force is a net shield between the nucleus and the core electrons. However, if a change in the oxidation number occurs in the valence shell (i.e., redistribution of molecular charge) the shielding effect of the valence electrons on the core electrons is thus decreased and the binding energy of the core electron increases.

The observed chemical shifts were interpreted in terms of an ionic model (also known as charged-shell model) described by Siegbahn (141) as follows:

"The atomic valence electron orbitals define a spherical valence shell of electric charge and the inner electrons, for instance the $1s$ electrons, reside inside this charged shell. If charge is added to or removed from the valence shell, as in the case when the atom is bound to other atoms in a molecule or a crystal, the electrical potential inside the valence shell is changed."

Thus if a charge $q$ is removed from the valence shell of an atom to infinity the potential energy of the inner electrons will decrease
by the amount and the binding energy will increase by the same amount

\[ \Delta E = \frac{1}{r} q \]  

(12)

where \( r \) is the radius of the orbital of the valence electron. Using the above equation, the change in energy expected to remove a unit charge from a distance of \( 1 \AA \) was found to be 11 eV. Since the observed shifts are smaller than this value, the electrostatic model was found to be much simplified.

The above free ion calculations were improved by taking into account the fact that the valence electrons are not transferred to or from infinite distance when a chemical bond is established. This is true in the case of ionic solids since the valence electron is moved only to some finite distance, on the counter-ion.

The above equation is then modified to give:

\[ \Delta E = \left( \frac{1}{r} - \frac{M}{R} \right) q \]  

(17)

where \( M \) is the Madelung constant, \( R \) the internuclear distance from the atom in question to its nearest neighbor. \( M \) is generally about 1.7 for most diatomic crystals when based on unit charges referred to the nearest neighbor distance. If \( R \) is taken to be about 5 a.u \( \Delta E = 5 \) eV. Although this number was found to be slightly large it was nevertheless approaching an appropriate value.

The above model is still much simpler because it assumed that the interactions between atomic electrons arise from the shielding effect of the outer electrons with no overlap of the atomic orbitals. The above assumption is known not to be valid.

An interesting result, however, of the above model is that it
showed that the chemical shifts of all core levels are the same because they are in a region of constant potential. This above result was confirmed experimentally in an investigation of iodine compounds by Fadley et al. They found that the shifts in the $3s$, $3p$, $3d$, $4s$, and $4p$ levels of iodine were equal within experimental error for KI0$_4$ and KI0$_3$: ($1.6 \pm 0.5$ eV for KI0$_3$ and $6.5 \pm 0.5$ eV for KI0$_4$ relative to KI).

More accurate calculations of chemical shifts (especially in organic molecules where the single electrostatic model does not hold very well) can be made by Hartree-Fock free ion-approximation, electronegativity (or Pauling Valence Bond approach) correlations, and CNDO charges correlation.

The results of the Hartree-Fock methods in general verify the qualitative conclusions given by the simple charged-shell model. Both these methods can be used to determine general trends in binding energy shifts. They both predict a decreasing chemical shift when one goes down a column in the periodic table. They also predict as mentioned above that the chemical shift varies little from one electron to another throughout the core and that when one goes across a row of the periodic table from left to right an increase in chemical shift of the same electron is observed.

The electronegativity approach is quite simple, it makes use of bond length and electronegativity to estimate the charge distribution among the bonds formed by the atom of interest. According to this model the charge $q_A$ on an atom $A$ is given by

$$q_A = Q_A + \Sigma I_n$$

where $Q_A$ is the formal charge on covalently bonded atom $A$. $I_n$ is
the partial ionic character summed over all the bonds involving atom A

\[ I_n = 1 - \exp[-0.25 (X_A - X_B)^2] \]  \hspace{1cm} (15)

where \( X_A - X_B \) is the electronegativity difference between atom A and atom B with which it is forming a bond.

For example for \( \text{SO}_4^{2-} \), \( Q_A \) is equal to -1.32 and \( q_A = +0.20 \). Correlations between \( q_A \) and binding energies were carried out for several compounds such as those of nitrogen (114), sulfur (152), carbon (151), arsenic (154) and selenium (153). The correlations seem to be quite good considering that they are only approximations and that the approach only takes into account the influence of the nearest neighbors. The method however has the advantage that it can be applied to any set of molecules for which complete octet structures can be written.

For more exact correlations of experimental binding energy shifts with charge, account has to be taken not only of the charge on the atom considered but also of the contribution to the potential at this atom caused by the charge of all other atoms in the system. This is done in the electrostatic molecular potential model (151, 152) in which the shifts are given by:

\[ \Delta E_i = k_q_i + V_i + 1 \]  \hspace{1cm} (16)

\[ V_i = \sum_{j \neq i} \frac{q_i}{R_{ij}} \]  \hspace{1cm} (17)

where

\( \Delta E_i \) = chemical shift of atom i

\( V_i \) = molecular potential at nucleus i

\( q_i \) = charge on atom i

\( R_{ij} \) = distance between nuclei i and j
\[ k = \text{a constant characteristic of the elements' inner level studied} \]

\[ l = \text{a constant depending on the choice of the reference level} \]

The magnitude of \( k \) is obtained from calculations on free atoms and ions.

From equations 16 and 17 one sees that if the atom charge and the molecular potential are linearly related, so also will be the chemical shift and the atom charge. Gelius, et. al (152) showed this to be true for a series of sulfur compounds.

The CNDO (complete neglect of differential overlap between atomic orbitals) molecular orbital method treats electron-electron repulsion specifically and yields the charge on the atom in consideration. This method gives slightly better correlation than the above two (155). However, it is lengthy and expensive.

Core electron shifts have also been successfully correlated with energies estimated from ground state thermochemical data by a method developed by Jolly and Hendrickson (156). It is based on the concept of equivalent cores, which implies that upon removal of an inner electron from an atom the valence electrons adjust as if the nuclear charge of the atom had increased by one unit. It is also assumed that atomic cores having the same charge are chemically equivalent. Chemical equations have to be written which have heats of formation equal to a given difference in binding energy. A good linear correlation was obtained for gaseous nitrogen compounds. The method, however, is not easily applicable to solid compounds because it is more difficult to write a chemical reaction having an energy equal to a given difference in binding energy, moreover thermodynamic data are often
lacking.

C. APPLICATIONS

1. **Elemental analysis**

   Qualitative elemental analysis is possible for all the elements in the periodic table (except hydrogen) since each element in a chemical compound makes a characteristic contribution to the electron spectrum. Knowing the position of the lines it is possible to identify the elements which generate them. Moreover photoelectron lines of adjacent elements in the periodic table are far apart so that overlap between lines from similar electrons of nearest neighbors does not usually occur.

2. **Quantitative analysis**

   The method has shown a potential for determining elemental ratios in a variety of organic and inorganic compounds. Siegbahn and co-workers analyzed brass samples containing zinc, copper, tin and lead (141). They have also determined the carbon-to-chlorine-to-sulfur ratios in a number of organic compounds and the carbon-to-chlorine-to-sulfur ratios in several amino acids and insulin (141). Their relative precision was about $\pm 5\%$. Recently Swartz and Hercules (147) developed a quantitative analytical procedure for bulk analysis of MoO$_2$-MoO$_3$ mixtures the quantitative analysis of the above mixture was found to be good to within one standard deviation of $\pm 2\%$. E.S.C.A. seems also to have some potential in gas analysis as shown by Siegbahn and co-workers (158).

3. **Structural analysis**

   This is the area of maximum applicability of the E.S.C.A. technique and where it competes and compliments other well established
methods such as IR, N.M.R., U.V., etc., for structural analysis.

One advantage of E.S.C.A. over the other methods is that the presence of an element is clearly established (from the binding energy) and then due to the occurrence of chemical shifts it is possible to determine in one molecule the different functional groups or chemical environments of that element.

The technique has been applied to organic as well as inorganic structure determinations with good results (141, 147-151).

It is also possible to determine the number of atoms of a given type in a molecule, from the ratio of the peak intensities for the element in question.

Chemical shifts have been tabulated for many elements in organic and inorganic compounds (141, 147-153) from these it appears that E.S.C.A. could clearly distinguish between types of inorganic nitrogen compounds such as nitrate, nitrite or cyanide. It is also possible to distinguish between compounds containing nitrogen-to-nitrogen or nitrogen-to-carbon bonds and those having nitrogen-to-oxygen bonds. The above is also true for many other elements for which correlation tables have been established, such as carbon, sulfur, phosphorous, selenium and boron (141, 147-153). The general features of E.S.C.A. pertaining to structural studies may be summerized as follows:

a) Core electron binding energies are characteristic of elements.

b) Core electron energy shifts reflect the charge on atoms in a molecule.

c) The shift of an atom in a molecule is, because of the small influence of secondary substituent effects, predominantly governed by the character of the nearest neighbor atoms and within narrow limits characteristic of structure elements or groups.
The contributions to the shift of an atom in a molecule from the bonds it forms can be regarded as additive and can be estimated either from the partial ionic character of bonds or from empirically derived group shifts.

In cases of strong conjugative or inductive effects, significant secondary shifts may occur.

Surface studies
Since the average escape depth of X-ray photoelectrons is around 100Å \((141, 159)\) E.S.C.A. is well suited for surface studies. Siegbahn and co-workers \((141)\) demonstrated that a surface can be studied even though it is covered by more than one layer of material. Moreover the technique seems to be quite sensitive in detecting even submonolayers on surfaces.

One of the significant applications of E.S.C.A. in this area is catalysis. Investigation of inhomogeneous catalysis has been explored by Delgass and co-workers \((159)\). They observed changes in the E.S.C.A. spectra of solid catalysts upon interaction with substrates (zeolites). They also observed chemical changes in an oxide surface after use as a catalyst.

Since the E.S.C.A. technique is presently under intense development new applications are appearing fast \((160)\). Most recent ones are those dealing with environmental pollution.

Chemical shifts for several arsenic compounds were determined by Hulett and Carlson \((161)\) in an attempt to study arsenic soil pollution.

Hulett, Carlson, Fish and Durham \((162)\) studied sulfur on the surfaces of particulate matter such as smoke particles and fly ash. They found that the E.S.C.A. technique can quite easily distinguish among sulfide, sulfate and sulfite.
A. **EQUIPMENT**

A Varian IEE-15 (induced electron emission) spectrometer was used. The simplified block diagram of the instrument is shown in fig. 35. The main components are:

1. **The X-ray source**

   A magnesium coated anode at 1253.6 eV, hidden from the tungsten cathode filament to minimize tungsten contamination.

2. **The sample compartment**

   It is surrounded by an aluminum window to avoid scattered electrons from the source entering the sample compartment, and to separate X-ray lines to desired band width. It is evacuated by a special non-magnetic titanium pump having a capacity of 400 l/sec. The sample is grounded and good contact is maintained between the spectrometer and the sample in order to avoid charging effects and to insure that the Fermi level of the spectrometer is the same as the one of the sample.

3. **The retarding voltage**

   The sweep/retarding voltage (step deceleration) is applied over a short distance preceeding the electron energy analyzer. Its function is to retard the initial electron energy from about 1100 V to around 100 V.

4. **The electron energy analyzer**

   It is a spherical electrostatic analyzer having a 10 cm radius and utilizing the whole sphere (360°). The design is shown schematically in fig. 36. It consists of two concentric spheres with a potential difference between them which could be varied from 10 to
Figure 35. Block Diagram of the Varian IEO-15 Spectrometer.

- X-ray power supply
- Sample inlet
- Retarding voltage
- Retarding voltage power supply
- Focus control
- Pulse preamp
- Analyzer
- Ionization gauge
- Gauge control
- Cold trap
- Mechanical pump
- Valve
- Hasting gauge
- Hasting pump
- Retarding voltage
- Scope
- Recorder
- Computer
- Counter
- Recorder
- Computer
- Scope
- Gauge control
- Cold trap
- Mechanical pump
- Valve
Figure 36. Schematic Diagram of the Electrostatic Electron Energy Analyzer.
100 eV and is kept constant during scan which is achieved by varying the retarding voltage. The analyzer is shielded from the earth's magnetic field by a double layer of mu-metal.

5. **The cylindrical condenser**

Here extraneous secondary electrons are eliminated and photoelectrons with specific kinetic energy are permitted to enter the detector.

6. **The detector**

Electron multiplier (15 dynodes). Beryllium-copper Venetian blind type.

7. **Data acquisition and readout**

It was handled by a Varian 620/i digital computer with 4-K memory (up to 2000 channels for accumulation of signals from repeated spectrometer scans). The computer also controls the entire operation of the instrument: element start voltage, scanning mode, data report and generation display.

8. **Operating conditions**

The experimental conditions are shown on the respective spectra. The peak positions are in eV and the spectra reproducibility is 0.03 eV. The carbon 1s line of graphite at 284 eV was used as reference to calibrate the spectra.

**B. AIR SAMPLING**

The air samples were collected by means of a high-volume air sampler from Gelman, over fiber-glass filter paper type A from Gelman Instruments.

The samples were collected outside the Coates Laboratories of Louisiana State University in Baton Rouge, Louisiana over a period
of 24 hrs. each, at an average flow rate of 80 c.f.m. The particulate concentration range was from 90 to 150 µg/m³.
RESULTS

Figs. 37, 38 and 39 display a typical spectrum of airborne particulate matter in the binding energy range of 10 to 100 eV, 100 to 300 eV, 300 to 500 eV respectively. Above each major peak observed, the element symbol is shown, followed in parentheses by the atomic orbital notation of the ejected electron and its spin quantum number.

The main elements identified from the E.S.C.A. spectra were: oxygen, aluminum, iron, silicon, sulfur, lead, chlorine, carbon, calcium and nitrogen. The most pertinent peaks from the point of view of air pollution studies were those for nitrogen, lead and sulfur.

A. NITROGEN

The nitrogen 1s signal shown in figs. 39, 40 and 41 appears to be complex indicating the presence of several different kinds of nitrogen. The spectrum in fig. 40 which was obtained by scanning for 20 min. shows at least two unresolved peaks at 399.4 eV and at 401.2 eV. The spectrum in fig. 41, which was obtained by scanning for 1 hr. shows an additional peak at 407.3 eV. The spectrum of ammonium nitrate a natural and common air pollutant (163) under the same experimental conditions consists of two photolines one at high binding energy (407.3 eV) for the nitrate nitrogen and the other line appearing at lower binding energy (402.5 eV) corresponds to the ammonium nitrogen. We can therefore assign the line at 407.3 eV in the spectrum of fig. 41 to the $\text{NO}_3^-$ ion and the line at 401.2 eV to the $\text{NH}_4^+$ ion. The assignment of the line at 399.4 eV is not
Figure 37. E.S.C.A. Spectrum of Airborne Particulate Matter from 10 to 100 eV.

Sweep width: 20 eV, Sweep time: 20 sec., Number scans: 60, Number channels: 100
Figure 38. E.S.C.A. Spectrum of Airborne Particulate Matter from 100 eV to 300 eV.
Sweep width: 20 eV, Sweep time: 20 sec.,
Number scans: 60, Number channels: 100.
Figure 39. E.S.C.A. Spectrum of Airborne Particulate Matter from 300 eV to 500 eV.

Sweep width: 30 eV, Sweep time: 20 sec.,
Number scans: 60, Number channels: 100
Figure 4.0. E.S.C.A. Spectrum of Nitrogen $1s$ in Airborne Particulate Matter (20 min. scan).

Sweep width: 10 eV, Sweep time: 70 sec., Number scans: 100,
Number channels: 100

Binding energy, eV
Figure 41. E.S.C.A. Spectrum of Nitrogen Is in Airborne Particulate Matter (60 min. scan).

Sweep width: 2 eV, Sweep time: 20 sec., Number scans: 100,
Number channels: 100

Binding energy, eV
straightforward. According to the charge corresponding to this binding energy, this photoelectron line would be associated with organic type nitrogen, with core charges on nitrogen close to zero.

According to Siegbahn (141), Hercules (149), Hendrickson, Hollander and Jolly (164), the nitrogen ls binding energies for various amino-type nitrogen is on the average 400 eV (the binding energy for pyridine is 398.5 eV). Consequently, we have tentatively assigned this peak to amino and pyridino type compounds.

B. LEAD

The doublets at 139.6 eV and 144.5 eV (figs. 38 and 42) are due to the lead 4f2 and 4f7/2 electron emissions. As seen in the spectrum of fig. 42, which was obtained after 30 min. scan, the lines appear to be relatively broad and their centers are shifted by 2.8 eV higher binding energy than elemental lead which gives peaks at 136.8 eV and 141.8 eV (141, 165). Hence it is suspected that the signals are not due to elemental lead but may be due to more than one lead compound.

To test this hypothesis the lead signals (in particular the one at 139.6 eV) were compared with those obtained from a synthetic mixture of PbCl₂ and PbO₂. This mixture was chosen because previous studies of automobiles exhaust speculated that lead may be present in the emission as a halide mixture which is partially converted into lead oxide in the atmosphere (166-168). The spectrum of the PbO₂ and PbCl₂ mixture is shown in fig. 43c.

Upon examination of the relatively broad 139 eV line it appears to be composed of two unresolved signals with a chemical shift separation of approximately 1 eV. As slightly more PbCl₂ is added to the mixture, the left hand side of this peak increased, indicating
Figure 42. E.S.C.A. Spectrum of Lead 4f in Airborne Particulate Matter.

Sweep width: 20 eV, Sweep time: 20 sec., Number channels: 100
Figure 43. E.S.C.A. Spectra of Lead for the Particulate Sample Plus Various Lead Compounds.

Sweep width: 20 eV, Sweep time: 20 sec., Number channels: 100
that the higher binding energy side corresponds to PbCl₂.

It should be noted that under the experimental conditions used, we were unable to distinguish between PbCl₂, PbClBr and PbBr₂. The PbCl₂ peaks therefore represent lead halide. The lead peaks from both the air sample (fig. 42) and the synthetic mixture (fig. 43c) have about the same line width and binding energies, which indicates that lead in the sample is probably present as a mixture of a lead halide and an oxide. It is also possible that other chemical forms of lead were present which were not resolvable under these experimental conditions. Among these, PbCO₃ is a strong possibility since it gives photoelectron peaks at 141.2 eV and 146.0 eV (169) (a shift of only 1.6 eV from PbO₂) and also because a recent study showed that lead carbonate is one of the major lead compounds in airborne lead particles along with lead oxide and the halides (117). Another possibility is PbSO₄, however this compound generates photo lines at 142.5 eV and 147.1 eV (169), and since these peaks appear at relatively higher binding energies than any of the lead peaks observed, we can conclude that virtually no lead sulfate was present in our sample.

The qualitative assessment of the relative amounts of the lead components were determined by the following two experiments.

The particulates sample was first lightly dusted with an extremely small amount of PbCl₂, which enhanced the higher binding-energy side of the line and caused a shoulder to appear on the lower binding energy side (fig. 43b). As PbCl₂ was added to the particulates sample it increased the halide component significantly over the oxide, thus explaining the decrease of the 139.6 eV peak width
and the appearance of the right side shoulder which is due to the oxide.

This experiment suggested that the concentrations of halide and oxide are of about the same order of magnitude in the air sample examined.

In the second experiment the particulates sample was dusted with PbO₂, which cause the disappearance of the shoulder or the lower binding energy side (fig. 43a). The disappearance of the shoulder on the right side follows since the oxide is now a major constituent of the mixture and not a minor one as in the first experiment. This once again confirms the conclusions drawn in the earlier experiment.

C. SULFUR

The sulfur 2p peak appears at 169.1 eV (figs. 38 and 44). This relatively high binding energy value for sulfur indicates that it is bonded to oxygen (141, 152).

From E.S.C.A. correlation tables for sulfur 2p compounds (152, 149) it was identified as the SO₄⁻ anion.

D. OTHER PEAKS IDENTIFIED

The silicon 2p₁/₂ peak at 103 eV (fig. 38) indicates a silicon to oxygen bond, the molecular structure was identified as SiO₂ (170).

The aluminum 2s₁/₂ peak at 119 eV (fig. 38) indicates the presence of aluminum in the +3 oxidation state (171), possibly indicating the presence of Al₂O₃.

The chlorine 2p₃/₂ line centered at 201 eV (fig. 38) indicates the presence of chloride (171).
Figure 44. E.S.C.A. Spectrum of Sulfur 2p in Airborne Particulate Matter.

Sweep width: 20 eV, Sweep time: 20 sec., Number scans: 50, Number Channels: 100
As demonstrated in the preceding pages, E.S.C.A. is a tool which can be used to identify the molecular forms of particulate pollutants in the atmosphere.

The occurrence of amino type compounds in association with airborne particulate matter is a quite interesting and new observation. Since compounds with these functional groups are utilized as gasoline additives, it seems that they come from emissions rather than by way of atmospheric reactions. The origin of ammonium in the particulates could be either direct emissions from automobiles exhaust which are known to emit the mixed ammonium lead halides (166, 167), or adsorption of NH$_3$ present in the atmosphere. A third possibility is the reaction of NH$_3$ with acidic gases in the atmosphere such as H$_2$SO$_4$ and HNO$_3$. A possible origin of the observed nitrate is adsorption of gas phase nitrates in the atmosphere on the particulates surface and/or oxidation of nitrogen compounds emitted as particles.

In the samples collected, sulfur existed almost entirely as sulfate. Virtually no SO$_2$ or sulfite was detected. This tends to indicate that most of the SO$_2$ in the atmosphere was adsorbed on the particles and subsequently converted possibly to (NH$_4$)$_2$SO$_4$. Another possibility is the direct oxidation of SO$_2$ to H$_2$SO$_4$ droplets which also adsorb on the particulates (108, 110).

Lead was observed in at least two forms, i.e., lead halide and lead oxide. Accurate identification is not possible at this time since the chemical shift for lead compounds is weak (169) and of the order of the resolving power of the presently used instrument.
Further research and development of the F.S.C.A. technique is needed in order to use it as a routine method for the determination of the chemical forms present in airborne particulates. The paucity of chemical shifts and of correlation tables for many elements hinders their positive identification at the present time.

The most vexing problem that faces E.S.C.A., however, is resolution. The maximum chemical shift for a given element is of the order of 4-10 eV and in most situations instrumental parameters permit a resolution of 1 to 2 eV. This is hardly high resolution spectroscopy!

However, even with the best instrumental resolution to come (possibly 0.2 eV or better) we still have to consider the natural broadening of the inner shell lines for the heavy elements (such as lead) which in the solid phase could be as high as 0.7 eV (172), obviously increased instrumental resolution would be of little help in this type of situation.

Despite the above hindering features E.S.C.A. has proved and is proving to be a very useful tool for chemists.


98. Wood, R.W., Phil. Mag., 27, 1018 (1914).


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EXAMINATION AND THESIS REPORT

Candidate: Yvon E. Araktingi

Major Field: Chemistry

Title of Thesis: Determination of Selected Atmospheric Pollutants by Atomic Fluorescence and X-Ray Photoelectron Spectroscopy

Approved:

[Signature]

Major Professor and Chairman

Max Goodrich
Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Date of Examination:

June 30, 1972