New Methods for the Determination of Trace Quantities of Vanadium.

Sham Lal Sachdev
Louisiana State University and Agricultural & Mechanical College

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by
Sham Lal Sachdev
B.S., Panjab University, 1959
M.S., Panjab University, 1960
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ABSTRACT

Occurrence of vanadium in a wide variety of material and its increasing number of applications have greatly emphasized the need for improved methods for its determination. Two new methods for the determination of trace quantities of vanadium have been developed; one based on atomic absorption spectroscopy and the other on the ring oven technique. The former is useful for the determination of vanadium in dilute solutions and the latter for smaller samples.

1. By Atomic Absorption Spectroscopy.

Although this recently developed technique has provided simple, sensitive and very selective methods for the determination of a large number of metals, it has not been very successful when applied to refractory metals such as vanadium. This is because vanadium forms very stable refractory oxides in the flame used for atomization and thus there are no free vanadium atoms left for atomic absorption. By the use of mixed systems of organic solvents in conjunction with a fuel rich oxy-acetylene flame, conditions have been found under which free vanadium atoms can be formed quite efficiently. Under these conditions atomic absorption spectroscopic technique has been found to provide a simple, sensitive, very selective and reliable method for the determination of vanadium. Sensitivity of the method is 0.72 mg/l (in organic phase) for 1% absorption. Vanadium is extracted as vanadium cupferrate into a mixture of oleic acid and methyl isobutyl
ketone. The organic phase is aspirated into a fuel rich flame of a Beckman integral aspirator type burner. The upper part of the inner luminous cone of the flame was found to be the best portion of the flame for the absorption of the $3183.9$ Å line of vanadium. The extraction procedure is simple and can also be used for concentrating vanadium from aqueous solutions. Vanadium concentrations as low as $1$ mg/l can easily be determined with reasonable accuracy.

2. By the Ring Oven Technique.

Ring oven methods of analysis are very useful when the quantity of test material available is very small. The method developed for the determination of vanadium is based on the selective reaction of $\alpha$-benzoinoxime with vanadium (V) in acidic medium. Selectivity of the method is further improved by extracting the precipitate formed between vanadium (V) and $\alpha$-benzoinoxime with benzene. The extraction is carried out on the filter paper placed on the ring oven. The method is simple, sensitive, selective and rapid. As little as $0.1\mu g$ of vanadium can be determined from a microliter drop of a solution.
CHAPTER I

INTRODUCTION

Vanadium, once regarded as a scarce element, is one of the more abundant elements of the minor constituents of the earth's crust and is more common than copper, lead, nickel or zinc. It is estimated (39) to be present to the extent of 0.015% in the earth's crust. In addition to about 70 vanadium minerals, this element is found in petroleum crudes (43), in some marine organisms, including holothurians and ascidians, in plants (48), and even in human teeth (60).

Recently, many unusual properties of vanadium and its compounds have been discovered. As a result, its applications are increasing rapidly. Vanadium metal makes hard alloys such as ferro-vanadium and nickel-vanadium. Pure vanadium metal is of great interest to the nuclear scientists for the following reasons:
1. It has relatively low neutron-capture cross-section.
2. It shows good strength at elevated temperatures in non-atmospheric conditions.
3. It does not alloy with uranium at high temperature.
4. It has good thermal conductivity.

Compounds of vanadium find their use in industry as catalysts for the manufacture of compounds such as sulfuric acid, phthalic anhydride and adipic acid. Large quantities of ammonium metavanadate
are applied in the formulation of ceramic glazes and stains. Vanadium compounds are also used in ink and paint industries because they contribute to drying characteristics. Compounds such as ammonium vanadyl tartarate are being examined for toxicity and if not toxic these may prove to be useful in the treatment of high blood pressure resulting from arteriosclerosis. The studies of Costello and Currani(7) have indicated that ingestion of vanadium compounds lowers the cholesterol level in human blood.

To keep in step with the increasing use of vanadium and its compounds, improved analytical methods for its detection and determination will be needed. This work has been undertaken with the aim of developing new and better methods for the determination of vanadium at microgram levels.
CHAPTER II

CONVENTIONAL METHODS FOR THE DETERMINATION OF VANADIUM

A. GRAVIMETRIC METHODS

Most organic and inorganic precipitants of vanadium are unsuitable for general use, either because they are not quantitative or because of coprecipitation of other elements along with vanadium. Thus, gravimetric procedures can only be used if the composition of vanadium solution is known and if appropriate separation procedures are employed. A six per cent aqueous cupferron solution has been recommended for the precipitation of vanadium (42). Mercurous nitrate and lead acetate have also been used as precipitants for the gravimetric determination (42).

B. TITRIMETRIC METHODS

Titrmetric procedures based on oxidation of vanadium (IV) to vanadium (V), as well as reduction of vanadium (V) to vanadium (IV), have been developed. In the case of solutions which contain no oxidizable element other than vanadium, the procedure is very simple. An acidic solution of tetravalent vanadium is titrated by means of a standard permanganate solution. To insure that vanadium in the sample solution is in the tetravalent state, excess ferrous ion is usually used and the excess subsequently oxidized by ammonium persulfate (24).
In place of ferrous ions, sulfur dioxide has also been used to reduce vanadium (V) to vanadium (IV). The excess of sulfur dioxide can be very easily removed by bubbling carbon dioxide vigorously through the sample solution. This procedure has been stated to be more accurate (21) than the method employing ferrous compounds as reductants.

The end point of these titrations may be determined visually, spectrophotometrically (18), or potentiometrically (15). Spectrophotometric methods for the determination of end points provide the most sensitive procedures. Such titration procedures have been successfully used for the determination of vanadium in steel samples.

Titrimetric procedures based on the reduction of vanadium(V) to vanadium (IV) have also been developed and used for the determination of vanadium in steel samples. In principle, vanadium is oxidized to the pentavalent state, excess oxidant is destroyed and the resultant solution is titrated against standard ferrous solution. Permanganate solution is often used to selectively oxidize vanadium(IV) and iron(II) without oxidizing chromium(III) which is a common interfering ion in the case of steel analysis. Excess permanganate is reduced by sodium nitrite which does not reduce vanadium (V). Excess nitrite must be destroyed and this can easily be done by the use of sulfamic acid or urea. The end point of such a titration can be determined by the use of an indicator such as barium diphenylaminesulphonate (33), potentiometrically (47), amperometrically (38) or by dead-stop determination of the end point (17). Potentiometric and amperometric methods for the determination of the end point have been reported to
be more precise than visual means, whereas, the dead-stop determination of the end point has been reported to be very precise. Large quantities of uranium, chromium and titanium can be tolerated in these procedures.

C. PHOTOMETRIC METHODS

Photometric procedures are quite sensitive and are very useful for the determination of vanadium at low levels of concentration. A number of spectrophotometric methods have been developed and are used in non-routine analysis. Some of the commonly used procedures have been listed as follows:

1. As Phosphotungstovanadate. Phosphoric acid intensifies the yellow color formed by the reaction of sodium tungstate with vanadium (V) and thus provides a sensitive method for the determination of vanadium (62). This procedure, however, is not very selective and therefore, elimination of interfering ions is necessary. The recommended procedure for the removal of interfering ions is by mercury cathode electrolysis. Selectivity may also be achieved by extraction with ethylmethyl ketone (23). A procedure based on this reaction has been reported for the determination of vanadium in low-alloy steel (6).

2. Spectrophotometric Determination with Hydrogen Peroxide. This procedure is less sensitive than the phosphotungstate method, but it is more selective (63). Only titanium, molybdenum, tungsten and chromium present interference. Titanium presents the greatest interference problem.
3. **Determination as 8-hydroxyquinolinate.** The complex formed between vanadium (V) and 8-hydroxyquinoline is extracted into alcohol-free chloroform (46). An ethylenediamine tetraacetic acid solution in the presence of calcium salt is used as a masking reagent to prevent the extraction of other interfering ions. The method is suitable for biological samples.

4. **Miscellaneous Photometric Methods.** A large number of photometric procedures have been developed using reagents such as pyrocatechol violet (29), rutin (10), xylenol orange (31), N-benzoyl-N-phenyl hydrazine (35), N-benzoyl tolyl hydroxylamine (30), and 4(2-pyridylazo)resorcinol (5). All of these spectrophotometric procedures are quite sensitive and desired selectivity can be achieved by the use of masking agents. The choice of masking agents will, by all means, depend upon the nature of interfering ions present.

D. **EMISSION SPECTROSCOPY**

Arc and spark spectra of vanadium are quite complex and provide many suitable lines for its determination. The complex nature of the spectra, however, increases the problems due to interference. Vanadium has been stated to show some 3130 neutral and singly ionized spectral lines (19). Thus, a spectrograph of high dispersion and resolution is required for the determination of vanadium. Some 12 spectrographic methods for determining vanadium have been suggested by A.S.T.M. (25). These methods include point to plane, porus-cup, pellet, rod to rod and rotating disc techniques. These procedures have proved to be very useful for the determination of trace quantities of vanadium in steel, aluminum and biological samples.
E. X-RAY FLUORESCENCE SPECTROSCOPY

Vanadium is at the lower fringe of the group of elements in the periodic table that are amenable to x-ray analysis. It emits a K\(_\alpha\) line of wave-length 2.502A. Procedures based on this principle have been developed for the determination of vanadium in cracking catalyst (11), petroleum (8), steel and carbonaceous materials (3).

F. NEUTRON-ACTIVATION ANALYSIS

When vanadium is bombarded with slow neutrons, the following \((n,\gamma)\) reaction occurs:

\[
\frac{^{51}\text{V}}{^{23}\text{O}} + _0^1\text{n} \rightarrow \frac{^{52}\text{V}}{^{23}\text{O}} - \gamma \rightarrow \frac{^{51}\text{V}}{^{23}\text{O}} + \frac{^{52}\text{Cr}}{^{24}\text{Cr}}
\]

The half life of \(\frac{^{52}\text{V}}{^{23}}\) is 3.75 minutes and this precludes isolation of the element after irradiation; thus, interference due to other elements undergoing the \((n,\gamma)\) reaction are to be expected. However, due to large activation cross-section for vanadium (4.5 barns) short irradiation times are possible and the activity of a large number of isotopes would be negligible in this case. Further elimination of interferences can be obtained by the use of a gamma spectrometer to monitor the gamma energies within a band ranging from 1.33 to 1.55 m.e.v. which includes 1.46 m.e.v. gamma radiation from \(\frac{^{52}\text{V}}{^{23}}\).

Neutron activation techniques have been applied for the determination of vanadium in graphite, high-alloy steel (27) and in petroleum (4).

G. POLAROGRAPHY

The study of several oxidation-reduction reactions of vanadium by polarographic means has resulted in useful methods for its
analysis (26). Procedures based on oxidation-reduction reactions of bivalent, trivalent, tetravalent and pentavalent vanadium have been developed. The recommended method for the removal of interference is by electrolysis, using a mercury cathode cell. Good results have been reported on a wide variety of steel samples (28).

H. FLAME PHOTOMETRY

The use of flame photometry for the determination of vanadium has been very limited because the characteristic line spectrum of atomic vanadium cannot be excited by ordinary flames. This is so because vanadium forms stable refractory oxides. Line spectra of vanadium can be excited by an oxygen-cyanogen flame (20). Oxygen-cyanogen flames are very bright, noisy and therefore inconvenient to work with. Procedures using a band spectrum of vanadium oxide, VO, have been developed (41, 45). In these procedures, there are several interferences encountered. Common elements like copper, iron, titanium, niobium and zirconium, which are likely to be found with vanadium interfere in such determinations (45).

I. SUMMARY

The choice of any analytical method is generally a compromise between several factors, such as speed, accuracy, sensitivity and precision. Gravimetric, volumetric and polarographic methods are macro methods. These are useful for the determination of large quantities of vanadium but cannot be used for the determination of vanadium if it is present in the milligram range or less. Colorimetry, spectrography, X-ray fluorescence and neutron activation provide various procedures for the determination of trace quantities of vanadium in a variety of materials. Among the colorimetric procedures, determination with
phosphotungstate and N-benzoylphenylhydroxylamine are useful down to about 10 mg/l levels. X-ray fluorescence and neutron activation analysis are also very useful for trace analysis of vanadium if interferences can easily be overcome. Emission spectrographic techniques are employed over a range of vanadium concentrations from trace to a few per cent.

A review of methods for the determination of vanadium clearly shows that simple, rapid, accurate, sensitive and selective procedures for the determination of vanadium will be quite valuable. The recently developed technique of atomic absorption spectroscopy gives promise of such a procedure for vanadium. This last technique is certainly not an alternative to a direct reading spectrograph. It can, however, supplement such a spectrograph for it is simple, rapid, sensitive, selective and suited for use by non-professional personnel. Already, methods are available for the determination of about thirty elements at parts-per-million levels. As a result of the work described, the technique can be used with confidence as a tool for the determination of trace amounts of vanadium.
CHAPTER III

ATOMIC ABSORPTION SPECTROSCOPY

A. HISTORICAL BACKGROUND

The phenomenon of atomic absorption and emission of radiant energy has been known for about one hundred years. During all these years, steady progress has been made in the development of emission methods of spectrochemical analysis whereas absorption methods have been largely confined to the studies of the composition of solar and stellar atmospheres.

Based on the principle of atomic absorption, Woodson (64) in 1939 designed and patented an instrument for the determination of mercury vapour in air. This, however, did not attract much attention and the potentialities of analytical methods based on this principle were completely ignored until 1955 when Walsh (49) demonstrated its applicability to a wide variety of analytical problems. Since then atomic absorption spectroscopy has been applied to determine trace quantities of a large number of elements in a variety of materials such as medicines, biological samples (e.g., blood, urine, saliva, tissue and spinal fluids), agricultural products, soils, plants, plant nutrients, foods, beverages, petroleum, metallurgical samples, water, air, cements, glass, paints and other chemicals.
B. THEORY

Atoms in the ground state constitute the bulk of an atomic population under most conditions. In this state atoms may absorb radiant energy of certain characteristic frequencies and be raised to excited states. During this process, electrons are moved from a lower energy level to a higher energy level and if the difference between these two energy levels is $h\nu$, where $h$ is Planck's constant, then $\nu$ will be the frequency of the radiation absorbed. This absorption of energy is proportional to the concentration of atoms in the ground state. Because small changes in temperature do not alter the concentration of atoms in the ground state appreciably, slight changes in temperature have no effect on the absorption.

The absorption coefficient at frequency $\nu$, $K_\nu$, is defined by:

$$I_\nu = I_{0\nu} \exp(-K_\nu l) \quad (1)$$

where $I_{0\nu}$ is the initial intensity of the incident parallel beam of monochromatic radiation and $I_\nu$ is the intensity after it has passed through the layer of absorbing medium of thickness $l$. The absorption coefficient is a function of frequency. But, no absorption line is infinitely narrow and no radiation source emits purely monochromatic radiation. Therefore, the absorption coefficient obtained in practice is the integrated absorption coefficient. The integrated absorption coefficient ($50\nu$) of atoms in a gaseous state is given by
the following relation:

\[
\int_0^{\infty} K_N \, dv = \frac{\pi e^2 \, N \, f}{mc} 
\]

(2)

where \( e \) is the electronic charge, \( m \) the electronic mass, \( c \) the velocity of light, \( N \) the number of atoms per \( \text{cm}^3 \) which are capable of absorbing the radiation frequency ranging from \( f \) to \( f + d \) and \( f \), the oscillator strength, is the average number of electrons per atom which can be excited by the incident radiation.

If there are \( N \) atoms per \( \text{cm}^3 \) capable of absorbing, then the total absorption \( A \) will be:

\[
A = \frac{\pi e^2 \, f \, N \, v \, l}{mc} 
\]

(3)

Atoms capable of absorbing are the ground state atoms and if the total concentration is to be measured it will be necessary to know the relationship between the ground state atoms and the total concentration of the atoms. According to Boltzman statistics the distribution of atoms in different energy states at temperature \( T \) is given by:

\[
N_j = \frac{N \, g_j \, \exp \left( -\frac{E_j}{kT} \right)}{\sum g_j \, \exp \left( -\frac{E_j}{kT} \right)} 
\]

(4)

Here \( N \) is the total number of atoms, \( N_j \) is the number of atoms in the \( j \)th state, \( g_j \) the statistical weight, \( E_j \) is the energy of the \( j \)th state and \( k \) is the Boltzman constant. Walsh (49) calculated the magnitude of the fraction of atoms in the first excited state for
resonance lines of various elements at temperatures ranging from 2000°K to 5000°K. His results show that in nearly all cases the number of atoms in the first excited state is only a small fraction of the number of atoms in the ground state. For example, the ratio of $N_j/N$ for the 2139 Å line of zinc at 2000°K is $7.29 \times 10^{-15}$, and for the same line at 5000°K is $4.32 \times 10^{-8}$. Equation 4 and the calculated results also show that the number of excited atoms varies exponentially with temperature whereas the number of atoms in the ground state remain virtually constant. Thus, small changes in temperature will effect the emission intensity which is proportional to the number of excited atoms. Because the number of ground state atoms does not vary much with temperature, slight changes in temperature will not effect the absorption. This is one of the principal advantages of atomic absorption photometry over flame emission photometry.

The shape of the atomic absorption line is determined by the following factors:

a. The natural width of the line, due to the finite lifetime of the excited state.

b. The Doppler broadening, due to the motion of the atoms relative to the observer.

c. Pressure broadening which is due to the reduction in the mean free time between collisions with other atoms.

d. Stark broadening, due to external electric fields.

The natural width of an atomic absorption line is of the order of $10^{-4}$ Å. Considering Doppler's shift at 2000°K, it is of the order of 0.01 Å. To isolate such a line from the continuous background, a
resolution of 500,000 will be required which is beyond the performance of most spectrographs. In addition, the energy emitted over such a small spectral slit-width will be too small to be measured accurately by photoelectric methods commonly used for the measurements of light intensity.

Walsh (49) demonstrated the possibility of accurate measurements of the absorption signal by the use of sharp line source. In such a case the only requirement is to isolate the line selected for analysis from other lines emitted by the source and this can easily be achieved by common monochromators.

In most instances, thermal excitation of the atoms gives rise to emission of radiation of the same frequency as the absorption line. This difficulty can be overcome by chopping the source radiation before it passes through the atomic vapor and amplifying the output of the detector with an amplifier tuned to the chopping frequency.

C. EQUIPMENT

There are about ten models of atomic absorption spectrophotometers commercially available. This includes single as well as double beam instruments. The following diagram would explain the basic components and their arrangement in a single beam assembly.

```
\begin{center}
\begin{array}{c}
\text{Source of radiation} \\
a
\end{array} \quad \begin{array}{c}
\text{Chopper} \\
b
\end{array} \quad \begin{array}{c}
\text{Means of atomization} \\
c
\end{array}
\end{center}
\begin{center}
\begin{array}{c}
\text{Detector} \\
e
\end{array} \quad \begin{array}{c}
\text{Monochromator} \\
d
\end{array}
\end{center}
Readout
a. **Sources of Radiation.** Requirements for a sharp-line source were discussed on the previous page. Hollow cathode lamps for a large number of elements are available in the market and constitute the most commonly used sources. However, in some cases like those of sodium, potassium and mercury, spectral vapour lamps may be more useful.

b. **Chopper.** When a beam of light, emitted from a hollow cathode lamp, is passed through the flame, and if appropriate metal atoms in the ground state are present in the flame, a fraction of light proportional to the concentration of metal atoms is absorbed. At the same time some atoms are thermally excited by the flame and emit radiation of the same frequency as the absorption line. A chopper is employed to eliminate this emission signal. The beam of incident radiation is chopped at definite time intervals. The amplifier in the readout assembly is tuned to the chopping frequency and therefore, reads only the change in the intensity of the light due to absorption and does not detect the emitted radiation since it is not modulated to the tuned frequency of the detector.

c. **Means of Atomization.** So far the most common means of reducing the sample to atomic vapour is by flame. Hydrogen, acetylene and methane are the commonly used fuels. Both air and oxygen are often used as supporters of combustion; air mostly in premixed type burners, and oxygen in integral total consumption burners. Currently, a great deal of work is being carried out to develop new and better means of atomization. Various fuel mixtures and other techniques for obtaining high temperatures such as plasma torches are being tried.
d. **Monochromator.** Because sharp line sources are used, an ordinary monochromator is quite sufficient. Either quartz prism or grating type monochromators may be used in these instruments.

e. **Detector and Readout.** Basic components of this unit are a photomultiplier tube and an amplifier tuned to the chopper frequency.

In this study, a Perkin Elmer model 303 atomic absorption spectrophotometer was used. This is a double beam assembly and the layout of basic components is as shown in Figure 1.

![Diagram](image)

**Figure 1**

- $M_1$ through $M_{12}$ - Mirrors
- D - Detector
- $S_1$ - A hollow cathode lamp
- $S_2$ - Slit
- F - Flame
- C - Chopper
- G - Grating
CHAPTER IV

DETERMINATION OF VANADIUM BY ATOMIC ABSORPTION SPECTROSCOPY

A. INTRODUCTION

The technique of atomic absorption spectroscopy has provided an elegant means for the determination of a large number of metals at the parts per million and parts per billion levels. The technique has not been successful when applied to refractory metals such as aluminum, niobium, tantalum, titanium, vanadium and zirconium, etc.

Elwell and Gidley in 1962 (12) listed vanadium as one of the elements which could not be determined by atomic absorption spectrophotometry. The reason for this failure of atomic absorption spectrophotometry when applied to vanadium seems to be the formation of stable refractory oxides of vanadium in the flame which thus leaves no free atoms for the atomic absorption. If the flame conditions are highly reducing so as to prevent the formation of refractory oxides in the reducing part of the flame, it would be possible to observe the absorption signal for vanadium atoms in this part of the flame.

Because the absorption of light signal is proportional to the population of metal atoms in the flame, attention is drawn towards the mechanism of the production of metal atoms in the flame. Robinson and Kevan (40) have explained, in general, the mechanism of the production of metal atoms as follows:
Flame has been considered to consist of the following four parts:

1. **Base.** In this part of the flame, droplets of the sample undergo evaporation. Important controlling factors for the atomic absorption may be the droplet size, nature of the solvent, the flame temperature and the feed rate.

2. **Inner Cone.** Here solid particles undergo disintegration. The controlling factors are the flame temperature and the composition of the flame surrounding these particles.

3. **Reaction Zone.** In this zone of the flame, atoms may undergo oxidation depending upon the flame composition and the stability of the metal oxide.

4. **Outer Mantle.** Here metal atoms are in equilibrium with the metal oxide. This equilibrium also depends upon the flame composition and the stability of metal oxide.

Obviously, in the case of refractory metals like vanadium, stable refractory oxides are formed in the reaction zone and under normal flame conditions these oxides are not decomposed in any part of the flame. It is clear from the discussion of mechanism for the production of metal atoms that the flame composition plays a very important role. Thus, it may be possible to detect vanadium by atomic absorption by using a hot and highly reducing flame for atomization. Fassel and Mossotti in 1963 (13) reported the possibility of determining vanadium and some other refractory metals by using fuel rich oxygen-acetylene flames and by feeding the metal solution in an organic solvent (ethanol). Radiation was passed through three flames
of Beckman integral type burners arranged in a row and sensitivity for vanadium has been reported to be 10 mg/l for 1% absorption. Slavin and Manning (44) confirmed the work of Fassel and Mossoti and reported a slightly better sensitivity (7 mg/l for 1% absorption) under similar conditions, using Zeiss total consumption burner. However, in such a flame, low signal/noise ratio prevented the determination of vanadium in dilute solutions.

Recently, Amos and Thomas (1) have reported a sensitive method for the determination of aluminum from aqueous solution by using a long-path premixed type oxy-acetylene burner. But, the possibility of frequent explosions while using an oxygen-acetylene mixture in a premixed type burner is a serious limitation. In order to overcome this difficulty, Willis (61) has suggested the use of a nitrous oxide-acetylene mixture in a premix type burner made of 3/8 inch thick stainless steel with a slot as large as 4 x 0.015 inch². The reported sensitivity for vanadium under these conditions is 1.5 mg/l for 1% absorption. The use of nitrous oxide instead of air or oxygen is considerably more expensive. A standard tank of nitrous oxide costs about $40.00 and lasts only 10 hours as compared to a tank of air or oxygen which costs about three to four dollars and lasts about 30 hours.

The work presented here has been carried out with an objective of improving the flame conditions such that the determination of vanadium from dilute solutions could be possible by means of atomic absorption spectroscopy. Conditions for a very selective and very sensitive method for the determination of vanadium have been
developed by feeding vanadium in a mixture of organic solvents to
a fuel rich oxygen-acetylene flame of a Beckman integral type aspirator
burner.

B. EXPERIMENTAL

All solutions were made in double distilled water.

1. Preparation of Standard Solutions of Vanadium. A stock solution,
10,000 mg/1, with respect to vanadium, was prepared by dissolving
22.80 g of pure ammonium metavanadate in about 100 ml of 50% sulfuric
acid and the volume made up to one liter with water. This solution
was stored in a polyethylene bottle. Various other concentrations
were prepared by diluting appropriate volumes of this solution.

2. Other Solutions. Solutions other than that of vanadium such as
that of cupferron and various interfering ions were prepared by
using a torsion wire balance and therefore may be regarded as approxi­
mate. All reagents used were of analytical grades.

C. APPARATUS

Atomic absorption spectrophotometer (Perkin-Elmer's model 303),
large bore-integral atomizer burners-oxygen/acetylene assembly
(Beckman Instrument, Inc., No. 4090), vanadium hollow cathode lamp
(Ransley Glass, Melbourne, Australia), a pair of tongs, several 5 ml
beakers, polyethylene bottles and separatory funnels, etc.

D. PROCEDURE FOR EXTRACTION

An aqueous solution of vanadium was mixed with 1/10th of its
volume of concentrated sulfuric acid and the resultant solution was
cooled in an ice bath. The ice cold solution was taken in a separa­
tory funnel of appropriate size and to this, 6% aqueous solution of
cupferron (N-nitrosophenylhydroxylamine ammonium salt) was added.
One milliliter of cupferron solution per milligram of extractable ion should be added. The mahogany red precipitate formed with vanadium(V) was extracted into an appropriate fixed volume of methyl isobutyl ketone (MIBK) or a mixture of MIBK and oleic acid. The solutions were shaken for at least one minute before separating the two phases.

E. PROCEDURE FOR THE STUDY OF INTERFERENCES

To 2.5 ml of ammonium metavanadate solution (1000 mg/l with respect to vanadium), 2.5 ml of interfering ion solution of 10,000 mg/l with respect to the interfering ion was added. This solution was mixed with 2.5 ml of concentrated sulfuric acid and the final volume was adjusted to 25 ml. This resulting solution, which contained 100 mg/l of vanadium and 1000 mg/l of interfering ion, was cooled to about 10°C. The solution was transferred to a separatory funnel and 5 ml of 6% aqueous cupferron solution was added. The precipitate formed was extracted into 25 ml of (22:78) mixture of oleic acid and MIBK. The atomic absorption of this solution was studied and compared with the absorption from a solution prepared in a similar manner, containing 100 mg/l of vanadium, but no interfering ion.

F. WATER ANALYSIS

To 50 ml of aqueous vanadium solution (1 mg/l to 5 mg/l with respect to vanadium), 5 ml of concentrated sulfuric acid was added. The solution was cooled in ice to about 10°C. The cold solution was transferred to a 100 ml separatory funnel and 1 ml of 6% aqueous cupferron solution followed by 5 ml of (22:78) mixture of oleic acid and MIBK were added. The mixture was shaken for one minute and the phases were allowed to separate. The organic phase was aspirated to the flame for absorption studies.
G. SETTING OF THE INSTRUMENT

1. Choice of Absorption Frequency. Fassel and Mossoti (13) studied the sensitivity of various absorption lines for vanadium. Their results are given in TABLE I.

<table>
<thead>
<tr>
<th>Wavelength, Å</th>
<th>Sensitivity (mg/l of vanadium for 1% absorption)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3183.41</td>
<td>25</td>
</tr>
<tr>
<td>3183.98</td>
<td>10</td>
</tr>
<tr>
<td>3185.40</td>
<td>25</td>
</tr>
<tr>
<td>3828.56</td>
<td>100</td>
</tr>
<tr>
<td>3840.75</td>
<td>100</td>
</tr>
<tr>
<td>3855.84</td>
<td>50</td>
</tr>
<tr>
<td>3902.25</td>
<td>100</td>
</tr>
<tr>
<td>4111.78</td>
<td>100</td>
</tr>
<tr>
<td>4379.24</td>
<td>50</td>
</tr>
<tr>
<td>4384.72</td>
<td>100</td>
</tr>
<tr>
<td>4389.97</td>
<td>100</td>
</tr>
</tbody>
</table>

A wavelength of 3183.98 Å has been selected as the most intense and sensitive for vanadium. The instrument used, however, is not capable of resolving this line from lines of wavelength 3183.41 Å and 3185.40 Å. For the use of the 3183.98 Å line, the wavelength dial should be set at this reading and the Range-switch should be set at "UV Range."
2. **Placement of the Hollow Cathode Lamp and Source Control.** After having fitted the hollow cathode lamp in the bracket provided, the bracket is fitted in its position in the lamp compartment on the left panel of the instrument. The lamp terminals are connected to the proper leads and the power switch is turned on. With the scale switch at position 1, amplifier gain at position 5 and the slit control at 3, the source control is turned clockwise until the needle on the energy meter is in the middle of the scale. The position of the bracket carrying the hollow cathode lamp is now adjusted so that the needle on the energy meter reads maximum. The fine wavelength control is adjusted in the same manner to obtain maximum reading on the energy meter.

3. **Choice of Lamp Current.** On each lamp, an optimum current for its operation is given and in the case of the vanadium lamp used in these studies, it was 20 mA. Although the manufacturer advises not to use more than the recommended current, it was necessary to use larger currents in these experiments in order to maintain a proper signal to noise ratio. It has been found that currents as high as 50 mA can be used for a short period without damaging the lamp. In these experiments, a lamp current of 30 mA has been used and was set with the help of source control until the ammeter in the lamp compartment read 30 mA. In view of the high signal/noise ratio, higher lamp currents are more desirable while using the highly reducing oxy-acetylene flame. This, however, may shorten the life of the lamp to some extent. A 30 mA current has been found to be very satisfactory with other settings as will be described. The lamp has been found to give good service even after sixty hours of use.
4. **Setting of the Scale Switch.** The scale switch provided on the left panel of the instrument has four positions; marked 1, 2, 5 and 10, which indicate the scale expansion. In all experiments reported here, the scale switch was set on position 1 which gave a direct reading of the percentage of signal that was absorbed. Greater scale expansion may be useful when absorption readings are very low.

5. **Setting of Gain-control.** The amplifier gain-control should be so adjusted that the needle of the energy meter stands in the middle. Setting of gain-control at positions higher than 6 generally causes electrical noise with resulting fluctuations in the null meter. This can be avoided by adjusting the lamp current or slit opening. In general, higher lamp currents allow lower gain setting for a given slit opening. During the experiments reported here, the gain-control was set between positions four and five.

6. **Slit Setting.** The slit control has positions 1 through 6. The slit opening at these positions is given in [Table II](#).

### TABLE II

<table>
<thead>
<tr>
<th>Slit Position</th>
<th>Slit Opening (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.03</td>
</tr>
<tr>
<td>2</td>
<td>0.10</td>
</tr>
<tr>
<td>3</td>
<td>0.30</td>
</tr>
<tr>
<td>4</td>
<td>1.00</td>
</tr>
<tr>
<td>5</td>
<td>3.00</td>
</tr>
<tr>
<td>6</td>
<td>10.00</td>
</tr>
</tbody>
</table>
Because a bright, reducing oxy-acetylene flame had to be used in these studies, the slit opening was kept at a minimum in order to decrease the flame background radiation falling on the photomultiplier tube. This minimum, however, depends upon the lamp current and the gain-control setting. In the experiments described, a slit position of 3 was found to be satisfactory.

7. **Range Switch Setting.** The range switch has two positions, VIS for visible range and UV for ultraviolet range. Its setting depends upon the wavelength of absorption line used for the analysis. For the work reported here it was set at the UV range.

8. **Phase Switch.** If blocking the light beam, by placing a paper or hand above the burner, makes the needle on the energy meter to deviate, the beam is out of phase. For phase corrections, the phase switch should be turned to the alternate position.

9. **Zero Control.** After lighting the burner, the needle on the null meter should be brought to the middle by adjusting the zero control.

10. **Absorption Measurement.** When the sample is fed to the flame and if it absorbs some of the radiation passing through the flame, the needle on the null meter is deflected. The needle is brought back to the middle by turning the absorption control clockwise and the percentage of light absorbed is read on the absorption counter.

11. **Burner Assembly.** A large bore, integral type, aspirator burner (Beckman Instruments, Inc., No. 4090) has been used instead of Perkin-Elmer's premix type burner which could not be used for oxy-acetylene flames. A special rack was fitted for the use of one or more Beckman burners in place of the Perkin-Elmer burner. The position of the
burner was so adjusted that the beam of radiation was passed through the upper part of the inner, luminous cone of the flame. Two stage regulators were used on the gas tanks and a flow meter in the gas lines. Various flow rates for oxygen and acetylene were used and the results obtained will be discussed in the next chapter.

Many experiments were performed for comparison purpose. Therefore, conditions for these experiments were kept identical and were roughly the optimum conditions for the observations being made. In all such experiments, solvent was used to set the zero of the instrument and absorption reading for the blank was subtracted from the absorption reading for the sample. Alternatively, blanks may be used for setting the instrument for zero absorption.
CHAPTER V

RESULTS AND DISCUSSION

A. STUDIES OF VARIOUS FLAMES AND THE EFFECT OF ORGANIC SOLVENTS

Preliminary experiments were performed to observe the absorption signal in oxygen-hydrogen flame under different conditions. No absorption could be observed using aqueous solution of ammonium metavanadate of 1000 mg/l concentration with respect to vanadium. Using vanadium solution in 90% ethanol containing 500 mg/l of vanadium, only a very weak loss of signal (about 3% absorption) could be observed in a highly reducing flame. The studies indicated that an oxygen-hydrogen flame is unsuitable for the determination of vanadium, apparently because such flames are not hot enough to produce an atomic vapour of vanadium.

Absorption of the 3183.98 Å line of vanadium could be easily observed by using a fuel rich oxy-acetylene flame. Organic solvents seem to enhance the absorption. The effect of additions of organic solvents such as methanol, ethanol and isopropanol on the absorption signal was studied in flames of various compositions. The results are shown in Figures 2, 3, and 4. The solutions used contained 1000 mg/l of vanadium. These results show that absorption is maximum in highly reducing flames and that the slope of the curve obtained with highly reducing flame falls down rapidly as the concentration of organic solvent is increased. Moreover, the maximum absorption was
Concentration of Vanadium = 1000 mg/l.

Flame Composition
flow rate (1/min)

<table>
<thead>
<tr>
<th></th>
<th>Oxygen</th>
<th>Acetylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>---</td>
<td>3.0</td>
<td>2.6</td>
</tr>
<tr>
<td>x-x</td>
<td>3.0</td>
<td>3.1</td>
</tr>
<tr>
<td>△-△</td>
<td>3.0</td>
<td>3.6</td>
</tr>
<tr>
<td>◇-◇</td>
<td>3.0</td>
<td>4.1</td>
</tr>
<tr>
<td>△-△</td>
<td>3.0</td>
<td>4.6</td>
</tr>
</tbody>
</table>

Percentage of Methanol (v/v)

Effect of Methanol On the Absorption of 3183.9 Å Line of Vanadium in Oxy-acetylene Flames of Various Compositions.
Concentration of Vanadium = 1000 mg/l

Flame Composition
flow rate (1/min)

<table>
<thead>
<tr>
<th>Oxygen</th>
<th>Acetylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>•-•</td>
<td>3.0</td>
</tr>
<tr>
<td>x-x</td>
<td>3.0</td>
</tr>
<tr>
<td>△-△</td>
<td>3.0</td>
</tr>
<tr>
<td>o-o</td>
<td>3.0</td>
</tr>
<tr>
<td>△-△</td>
<td>3.0</td>
</tr>
</tbody>
</table>

Percentage Ethanol (v/v)

Figure 3

Effect of Ethanol on the Absorption of 3183.9 Å Line of Vanadium in Oxy-acetylene Flames of Various Compositions
Effect of Propanol-2 on the Absorption of 3183.9 Å Line of Vanadium in Oxy-acetylene Flames of Various Compositions
observed when the solution contained more than 70% of the respective organic solvent. This suggested that organic solvents are definitely playing an important role in the establishment of flame conditions. The flame is of more reducing character when larger quantities of organic solvents are used. Although flame could be made more reducing by increasing the flow rate of the fuel gas, this results in incomplete combustion and the flame does not provide enough energy for atomization of the vanadium. At the same time, unburned carbon particles physically scatter the incident radiation.

High concentrations of organic solvents yielded better absorption signals and this indicated the possible advantage of using an extraction procedure. A good extraction procedure would not only provide an organic medium for vanadium, it would also increase the selectivity of the method by eliminating a large number of possible interfering ions. In addition, a solvent extraction step would serve to concentrate vanadium in the organic solvent from a very dilute aqueous solution.

B. CHOICE OF EXTRACTION PROCEDURE

A good extraction procedure should be simple, selective and quantitative. In general, selectivity and quantitative extractability are more important factors than simplicity. In the case of atomic absorption, however, simplicity and quantitative efficiency would be more desirable, because the procedure itself is quite selective. Bearing this in mind the following extraction procedures for the extraction of vanadium were examined.
1. **As 8-hydroxyquinolinate.** Vanadium (V) can be quantitatively extracted from aqueous solution at pH 5 with 1% 8-hydroxyquinoline in chloroform. Addition of a masking solution consisting of EDTA and calcium acetate eliminates a large number of interferences. However, chlorinated solvents are undesirable for use in flames due to the formation of chlorine gas. This procedure, therefore, would not be the best choice for atomic absorption spectroscopy. Ethyl acetate or MIBK could be used for the extraction, but quinolinates have a tendency to decompose on warming and would thus clog the capillary of the burner. Moreover, a careful adjustment of pH is required which decreases the desirable simplicity of the procedure.

2. **Extraction Using a TTA/N-butanol System.** Extraction of vanadium with 2-thonyl trifluoroacetone (TTA) in normal butyl alcohol at pH 3.4 was examined. This procedure has been reported to be selective and ions such as Fe+3, Cr+3, Ti+4, Zr+4, As+3, Co+3, Ni+2, Nb+5, Ce+4 and Mn+2 are not extracted. Unfortunately, quantitative extraction was not achieved in a single step and this ruled out the possibility of using this procedure.

3. **Extraction as Cupferrate.** Extraction of vanadium as cupferrate in methyl isobutyl ketone (MIBK) from (1+9) sulfuric acid solution has been found to be very useful for these investigations. This procedure is simple and quantitative separations even at microgram levels can be obtained in a single extraction. Ethyl acetate or diethyl ether can also be used for extracting vanadium cupferrate, but, MIBK is more suitable for flame studies because it has a higher boiling point and the rate of its aspiration is also higher.
4. **Tridecyl Phosphine Oxide Method.** Vanadium (V) can be quantitatively extracted from a solution that is 0.5M with respect to sulfate and 1M with respect to nitrate by shaking with 0.4M tridecyl phosphine oxide in kerosene (34). Such a solvent would be desirable for establishing reducing conditions in the flame without lowering the flame temperature to a large extent. But, different samples of kerosens may contain varying amounts of vanadium as impurity and this would have to be taken into account.

C. **ENHANCEMENT OF ABSORPTION SIGNAL BY THE USE OF MIBK**

Absorption signals were found to be greatly enhanced when vanadium was aspirated to the flame as vanadium cupferrate in MIBK. Results for a solution containing 1000 mg/l of vanadium are given in TABLE III. The data for other solvents are also supplied for comparison purpose.

**TABLE III**

<table>
<thead>
<tr>
<th>Concentration of Vanadium (mg/l)</th>
<th>Solvent Used</th>
<th>Boiling Point (°C)</th>
<th>Percentage Absorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>Acetone</td>
<td>56.2</td>
<td>26</td>
</tr>
<tr>
<td>1000</td>
<td>Methanol</td>
<td>64.7</td>
<td>29</td>
</tr>
<tr>
<td>1000</td>
<td>Ethanol</td>
<td>78.4</td>
<td>33</td>
</tr>
<tr>
<td>1000</td>
<td>Propanol-2</td>
<td>82.4</td>
<td>43</td>
</tr>
<tr>
<td>1000</td>
<td>MIBK</td>
<td>118</td>
<td>57</td>
</tr>
</tbody>
</table>
These results indicate that solvents with high boiling points may be useful for developing a sensitive method for the determination of vanadium by atomic absorption. Consequently, solvents like glycol and glycerol, which have very high boiling points as compared to many other organic solvents, were tried. But in these cases very insignificant absorption was observed. Aqueous solutions containing 400 mg/l of vanadium with (a) 20% glycol and (b) 20% glycerol showed only 10% and 11.4% absorption respectively. However, considerable enhancement in the absorption signal was observed when compounds with high boiling points and long carbon chains like oleic acid were mixed with the MIBK used for extracting vanadium cupferrate. The effect of adding oleic acid, linoleic acid or linolinic acid on the absorption signal of vanadium was studied and the results are given in TABLE IV. Vanadium was extracted as vanadium cupferrate into a mixture of MIBK and fatty acid (80:20 by volume). Absorption readings were taken under optimum conditions.

### TABLE IV

**EFFECT OF MIXED ORGANIC SOLVENTS**

<table>
<thead>
<tr>
<th>Concentration of Vanadium (mg/l)</th>
<th>Solvent 80%</th>
<th>Mixture 20%</th>
<th>Percentage Absorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>MIBK + Oleic Acid</td>
<td>32.0</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>MIBK + Linoleic Acid</td>
<td>27.4</td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>MIBK + Linolinic Acid</td>
<td>24.5</td>
<td></td>
</tr>
</tbody>
</table>
The presence of about 20% (v/v) oleic acid in MIBK showed a six to seven fold increase in the absorption signal. TABLE IV also shows that increasing the amount of unsaturation in the fatty acid chain does enhance the absorption signal.

Although oleic acid is miscible with MIBK in all proportions, larger concentrations of oleic acid cannot be used because its high viscosity considerably lowers the rate of aspiration of the burner. Optimum conditions have been established by studying the absorption of vanadium as cupferrate in MIBK containing varying concentrations of oleic acid. Studies have been made with flames of four different compositions. Results are shown in Figure 5, where the absorption measurements have been plotted against the increasing concentration of oleic acid in MIBK containing 100 mg/l of vanadium as cupferrate.

The effect of adding oleic acid to vanadium in methanol, ethanol and propanol-2 has also been studied because these solvents have been reported to have been used in such studies. Results are shown in Figures 6, 7, and 8. The optimum concentration of oleic acid and the flame conditions have been found to vary slightly in all three cases. Approximately five to six fold enhancement of the absorption signal is observed upon the addition of about 20 to 26% (V/V) oleic acid to these solvents.

These studies show that the use of a solvent mixture containing 22% oleic acid and 78% MIBK (V/V) would be more useful for atomic absorption studies than MIBK alone. Although enhancement of the absorption signal was quite significant when oleic acid was added to
Concentration of Vanadium = 100 mg/l

Flame Composition
flow rate (1/min)

<table>
<thead>
<tr>
<th>Oxygen</th>
<th>Acetylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>♣-♣</td>
<td>3.5</td>
</tr>
<tr>
<td>x-x</td>
<td>3.5</td>
</tr>
<tr>
<td>o-o</td>
<td>3.5</td>
</tr>
<tr>
<td>Δ-Δ</td>
<td>3.5</td>
</tr>
</tbody>
</table>

Percentage of Oleic Acid Added to MIBK (v/v)

Absorption (%)

0  5  10  15  20  25

Effect of Addition of Oleic Acid to MIBK Used for Extracting Vanadium Cupferrate, on the Absorption of 3183.9 Å Line of Vanadium in Oxy-acetylene Flames of Various Compositions.
Concentration of Vanadium = 200 mg/l

Flame Composition
flow rate
Oxygen Acetylene

A - a
X - X
20' o-o
119 x- x
98 ▲ - ▲
84 o-o
327 10-
348 ▲ - ▲
439 15-

Percentage of Oleic Acid in Methanol (v/v)

Absorption (%)

Figure 6

Effect of Addition of Oleic Acid to the Solution of Vanadium in Methanol on the Absorption of 3183.9 Å Line of Vanadium in Oxy-acetylene Flames of Various Compositions.
Flame Composition flow rates (1/min)

<table>
<thead>
<tr>
<th>Oxygen</th>
<th>Acetylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.0</td>
<td>3.1</td>
</tr>
<tr>
<td>4.0</td>
<td>3.6</td>
</tr>
<tr>
<td>4.0</td>
<td>4.6</td>
</tr>
<tr>
<td>4.0</td>
<td>5.1</td>
</tr>
</tbody>
</table>

Percentage of Oleic Acid in Ethanol (v/v)

Figure 7

Effect of Addition of Oleic Acid to the Solution of Vanadium in Ethanol on the Absorption of 3183.9 Å Line of Vanadium in Oxy-acetylene Flames of Various Compositions
Effect of Addition of Oleic Acid to the Solution of Vanadium in Propanol-2 on the Absorption of 3183.9 Å Line of Vanadium in Oxy-acetylene Flames of Various Compositions.
methanol, ethanol or propanol-2, total absorption from such systems was quite low as compared to the oleic acid-MIBK system. Therefore, further studies of these systems were not continued.

D. ROLE OF THE ORGANIC SOLVENTS

The absorption of light signal is proportional to the population of ground state metal atoms in the flame. The enhancement of absorption signal associated with the use of organic solvents indicates an increased population of ground state metal atoms in the flame. Methyl isobutyl ketone is not only a good solvent for extracting vanadium cupferrate, it also has a lower viscosity and therefore higher aspiration rate than that of an aqueous solution. Higher aspiration rate means that more analyte goes into the flame per unit time which would increase the population of metal atoms in the flame. The use of the organic solvent also provides better reducing conditions in the flame which are necessary in the study of refractory metals. Also, the flame temperature is higher due to the heat of combustion of the solvent and this improves the sensitivity. In the case of aqueous samples, water has a cooling effect on the flame. The increase of aspiration rate and small differences in flame temperature, however, cannot account for the many fold increase of the absorption signal observed in many cases. The pattern of combustion of organic solvents and the droplet size formed also seem to be important controlling factors for atomization. Further enhancement of the absorption signal by the addition of oleic acid to MIBK indicates that the combustion pattern must be playing an important role in the process of atomization, because the addition of oleic acid actually
decreases the aspiration rate. The increased efficiency of atomization may be due to further disintegration of tiny droplets of oleic acid containing vanadium, higher flame temperature, etc.

Because various physical and chemical properties such as surface tension, viscosity, vapour pressure, heat of combustion, etc., influence the atomization efficiency, the effect of organic solvents is very hard to interpret in a direct atomizer-burner flame. The solvent effect can therefore vary a great deal with the conditions and thus the experimental results obtained under one set of conditions may not be valid for another.

E. OPTIMUM CONDITIONS

Absorption for vanadium, from solvent mixture containing 22\% oleic acid and 78\% MIBK (V/V), was measured in some 30 different compositions of oxy-acetylene flames. Results are shown in TABLES V, VI and VII. All measurements were made with flames in optimum position, that is, the absorption reading in each case was the maximum that could be obtained under the given flame conditions.

From the data shown in TABLES V, VI and VII, it is evident that an oxygen flow rate of 3.5 l/min with an acetylene flow rate of 3.3 l/min provides the optimum flame conditions for maximum absorption per unit concentration of vanadium. It may also be noted that noise level, which is oscillation of the needle about the null point, expressed as percentage absorption, is also quite low. A low noise level is very important for better precision and reproducibility of the method.
TABLE V

Absorption of 3183.9 Å Line of Vanadium

In Oxy-acetylene Flames of Different Compositions

Solvent Used: Mixture of Oleic Acid and MIBK (22:78 V/V)

Concentration of Vanadium: 200 mg/l

<table>
<thead>
<tr>
<th>Oxygen Flow Rate (1/min)</th>
<th>Acetylene Flow Rate (1/min)</th>
<th>Absorption (percent)</th>
<th>Noise Level (% abs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>2.05</td>
<td>17.6</td>
<td>1.60</td>
</tr>
<tr>
<td>3</td>
<td>2.31</td>
<td>27.6</td>
<td>1.60</td>
</tr>
<tr>
<td>3</td>
<td>2.56</td>
<td>46.4</td>
<td>2.45</td>
</tr>
<tr>
<td>3</td>
<td>2.82</td>
<td>50.9</td>
<td>5.20</td>
</tr>
<tr>
<td>3</td>
<td>3.08</td>
<td>51.2</td>
<td>5.20</td>
</tr>
<tr>
<td>3</td>
<td>3.33</td>
<td>49.0</td>
<td>5.20</td>
</tr>
<tr>
<td>3</td>
<td>3.59</td>
<td>44.6</td>
<td>4.10</td>
</tr>
<tr>
<td>3</td>
<td>3.85</td>
<td>41.2</td>
<td>3.52</td>
</tr>
<tr>
<td>3</td>
<td>4.10</td>
<td>37.2</td>
<td>2.45</td>
</tr>
</tbody>
</table>

Lamp Current Used = 30 mA.

Slit Opening = 0.3 mm.

Vanadium extracted as Vanadium cupferrate
TABLE VI

Absorption of 3183.9 Å Line of Vanadium in Oxy-acetylene Flames of Different Compositions.

Solvent Used: Mixture of Oleic Acid and MIBK (22:78 V/V)

Concentration of Vanadium: 200 mg/l

<table>
<thead>
<tr>
<th>Oxygen Flow Rate (1/min)</th>
<th>Acetylene Flow Rate (1/min)</th>
<th>Absorption (percent)</th>
<th>Noise Level (% abs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5</td>
<td>2.03</td>
<td>9.6</td>
<td>1.1</td>
</tr>
<tr>
<td>3.5</td>
<td>2.31</td>
<td>16.5</td>
<td>1.6</td>
</tr>
<tr>
<td>3.5</td>
<td>2.56</td>
<td>31.9</td>
<td>1.6</td>
</tr>
<tr>
<td>3.5</td>
<td>2.82</td>
<td>43.0</td>
<td>2.0</td>
</tr>
<tr>
<td>3.5</td>
<td>3.08</td>
<td>55.3</td>
<td>2.0</td>
</tr>
<tr>
<td>3.5</td>
<td>3.33</td>
<td>60.9</td>
<td>1.6</td>
</tr>
<tr>
<td>3.5</td>
<td>3.59</td>
<td>60.2</td>
<td>1.1</td>
</tr>
<tr>
<td>3.5</td>
<td>3.85</td>
<td>58.5</td>
<td>1.1</td>
</tr>
<tr>
<td>3.5</td>
<td>4.10</td>
<td>53.2</td>
<td>1.1</td>
</tr>
<tr>
<td>3.5</td>
<td>4.36</td>
<td>48.7</td>
<td>1.1</td>
</tr>
</tbody>
</table>

Lamp Current Used = 30 mA.

Slit Opening = 0.3 mm.

Vanadium extracted as Vanadium cupferrate
TABLE VII

Absorption of 3183.9 Å Line of Vanadium

in Oxy-acetylene Flames of Different Compositions.

Solvent Used: Mixture of Oleic Acid and MIBK (22:78 V/V)

Concentration of Vanadium: 200 mg/l

<table>
<thead>
<tr>
<th>Oxygen Flow Rate (1/min)</th>
<th>Acetylene Flow Rate (1/min)</th>
<th>Absorption (percent)</th>
<th>Noise Level (% abs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>2.56</td>
<td>4.6</td>
<td>0.60</td>
</tr>
<tr>
<td>4</td>
<td>2.82</td>
<td>6.5</td>
<td>0.60</td>
</tr>
<tr>
<td>4</td>
<td>3.08</td>
<td>11.0</td>
<td>1.10</td>
</tr>
<tr>
<td>4</td>
<td>3.33</td>
<td>14.1</td>
<td>1.60</td>
</tr>
<tr>
<td>4</td>
<td>3.59</td>
<td>20.0</td>
<td>2.45</td>
</tr>
<tr>
<td>4</td>
<td>3.86</td>
<td>25.6</td>
<td>2.45</td>
</tr>
<tr>
<td>4</td>
<td>4.10</td>
<td>46.8</td>
<td>3.52</td>
</tr>
<tr>
<td>4</td>
<td>4.36</td>
<td>53.5</td>
<td>3.52</td>
</tr>
<tr>
<td>4</td>
<td>4.62</td>
<td>56.1</td>
<td>3.52</td>
</tr>
<tr>
<td>4</td>
<td>4.88</td>
<td>56.0</td>
<td>4.10</td>
</tr>
<tr>
<td>4</td>
<td>5.12</td>
<td>51.0</td>
<td>4.10</td>
</tr>
</tbody>
</table>

Lamp Current Used = 30 mA.

Slit Opening = 0.3 mm.

Vanadium extracted as Vanadium cupferrate
As considered in the previous chapter, the population of the ground state vanadium atoms will not be the same in all parts of the flame. Therefore, absorption of radiation will also be different in different parts of the flame. Various parts of the flame, of composition mentioned above, were examined. Results are shown in TABLE VIII and Figure 9.

Lateral displacement of the burner along the path of the light beam did not affect the absorption so long as the beam of light was passing through the proper part of the flame.

F. USE OF MULTIPLE BURNERS

A turbulent flow burner system consisting of three Beckman 4090 atomizer burners (large bore-oxygen/acetylene assembly) mounted in a row are commercially available and are commonly used with the Beckman atomic absorption accessory and the Jarrel-Ash atomic absorption spectrophotometer. Such a system was used by Fassel and Mossoti (13) for observing the absorption signal of vanadium and certain other refractory metals. Absorption studies for vanadium were made using the system developed with one, two and three burners respectively. The results are shown in Figure 10. This figure shows three calibration curves obtained using one, two and three burners respectively. Considerable enhancement of the absorption signal has been achieved by the use of three burners in a row, and a resultant sensitivity of 0.72 mg/l for one per cent absorption was obtained. While using two or three burners in a row, oxygen and acetylene flow has to be adjusted such that each burner takes about 3.5 l/min of oxygen and 3.3 l/min of acetylene.
**TABLE VIII**

Absorption of 3183.9 Å Line of Vanadium at Different Heights in Oxy-acetylene-Flame.

Solvent Used: Mixture of Oleic Acid and MIBK (22:78 V/V)

Oxygen Flow Rate: 3.5 l/min

Acetylene Flow Rate: 3.33 l/min

<table>
<thead>
<tr>
<th>Height of the Light Beam From the Tip of the Burner (cm.)</th>
<th>Absorption (percent)</th>
<th>Noise Level (% abs.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.0</td>
<td>2.0</td>
<td>5.20</td>
</tr>
<tr>
<td>1.5</td>
<td>18.8</td>
<td>2.45</td>
</tr>
<tr>
<td>2.0</td>
<td>43.5</td>
<td>2.10</td>
</tr>
<tr>
<td>2.5</td>
<td>55.0</td>
<td>1.60</td>
</tr>
<tr>
<td>3.0</td>
<td>59.5</td>
<td>1.60</td>
</tr>
<tr>
<td>3.5</td>
<td>59.2</td>
<td>1.60</td>
</tr>
<tr>
<td>4.0</td>
<td>54.7</td>
<td>2.10</td>
</tr>
<tr>
<td>4.5</td>
<td>47.7</td>
<td>2.92</td>
</tr>
<tr>
<td>5.0</td>
<td>39.2</td>
<td>2.45</td>
</tr>
</tbody>
</table>

Lamp Current Used = 30 mA.

Slit Opening = 0.3 mm.

Vanadium extracted as Vanadium cupferrate
Concentration of Vanadium = 200 mg/l

Flow Rates
Oxygen Acetylene
3.5 1/min 3.3 1/min

Vanadium Present as Vanadium Cupferrate

Effect of Variation of Burner Height on the Absorption of 3183.9 Å Line of Vanadium.

Figure 9
Obtained with one Beckman Burner

 Obtained with two Beckman Burners

 Obtained with three Beckman Burners

Sensitivity

1. 2.1 mg/l (for 1% absorption)
2. 1.08 mg/l (for 1% absorption)
3. 0.72 mg/l (for 1% absorption)

Concentration of Vanadium (mg/l)

Figure 10

Calibration Curves
G. STUDY OF INTERFERENCES

The use of the extraction procedure eliminates a large number of possible interferences by cations and anions. The following cations, however, may be extracted along with vanadium (V) under the conditions described for the extraction. Their effect on the absorption of 3183.9 Å line of vanadium was studied. Results are shown in TABLE IX.

The presence of an excess of cupferron is desirable in all the cases and it is essential if iron, bismuth or antimony is present because these ions are preferentially complexed under the given conditions. Zirconium forms a white precipitate which can be very easily removed by passing the solution through a funnel with its stem plugs with glass wool.

H. PROCEDURE FOR THE ANALYSIS OF VANADIUM IN WATER SAMPLES

A method is described which is very suitable for the determination of vanadium in water samples. Vanadium concentrations as low as 1 mg/l can be very easily determined. Fifty milliliters of water containing 1 mg/l of vanadium was taken, the vanadium was extracted into 5 ml of mixed organic solvent (oleic acid + MIBK, 22:78 V/V) as vanadium cupferrate and was determined using a two-burner assembly. The method described is quite accurate and reproducible. Results of a few analyses are shown in TABLE X.
TABLE IX
Effect of Interfering Ions on the Absorption of 3183.9 Å Line of Vanadium

Concentration of Vanadium: 100 mg/l
Concentration of Interfering Ion: 1000 mg/l

<table>
<thead>
<tr>
<th>Interfering Ion Present</th>
<th>Absorption in Presence of Interfering Ion (percent)</th>
<th>Absorption Without Interfering Ion (percent)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb+³</td>
<td>40.6</td>
<td>40.5</td>
</tr>
<tr>
<td>Cu+²</td>
<td>39.9</td>
<td>40.5</td>
</tr>
<tr>
<td>WO₄⁻²</td>
<td>39.7</td>
<td>40.5</td>
</tr>
<tr>
<td>Bi+³</td>
<td>41.3</td>
<td>40.5</td>
</tr>
<tr>
<td>Th⁺⁴</td>
<td>40.6</td>
<td>40.5</td>
</tr>
<tr>
<td>MoO₄⁻²</td>
<td>41.3</td>
<td>40.5</td>
</tr>
<tr>
<td>UO₂⁺²</td>
<td>41.4</td>
<td>40.5</td>
</tr>
<tr>
<td>Sn⁺⁴</td>
<td>39.8</td>
<td>40.5</td>
</tr>
<tr>
<td>Ti⁺⁴</td>
<td>39.9</td>
<td>40.5</td>
</tr>
<tr>
<td>Fe⁺³</td>
<td>39.9</td>
<td>40.5</td>
</tr>
<tr>
<td>Zr⁺⁴</td>
<td>40.3</td>
<td>40.5</td>
</tr>
<tr>
<td>Vanadium Taken (mg/l)</td>
<td>Number of Determinations</td>
<td>Vanadium Found (mg/l)</td>
</tr>
<tr>
<td>-----------------------</td>
<td>--------------------------</td>
<td>-----------------------</td>
</tr>
<tr>
<td>1</td>
<td>10</td>
<td>1.03 ± 0.06</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>3.10 ± 0.09</td>
</tr>
</tbody>
</table>
A. INTRODUCTION

The first paper describing the ring oven technique was published by Weisz in 1954 (53). Originally, this method was developed as a qualitative separation technique for extremely small samples. Soon after its introduction, applications began to appear in various other branches of analytical chemistry. Qualitative and quantitative as well as inorganic and organic studies have now been developed.

Lack of sufficient test material is frequently a disadvantage, especially when complex mixtures are to be studied. The ring oven is a simple apparatus which has proved to be useful for the detection and determination of various elements by chemical methods where only very small quantities of test material are available. The ring oven not only enables one to concentrate the test material into a ring of very small area, it also makes possible the application of separation techniques such as solvent extraction and precipitation to very small quantities of test material (in the nanogram to microgram range). The method has found application in the following fields of analysis.

B. QUALITATIVE ANALYSIS

(1) Metal ions: Filter paper has been commonly used for spot reactions in cases where the reaction product is either a colored
insoluble product or has a pronounced tendency to adsorb on the filter paper. Where the reaction product does not meet these requirements, spot tests may be carried out on a spot plate in a small test tube, so that the presence of the reaction product can be determined. The ring oven can, however, be used to concentrate the reaction product in a small ring area, and thus enhance the sensitivity of the test.

West and Mukherji (58) have developed a procedure for the separation and microidentification of as many as 35 metal ions in a single drop of test solution. Their procedure combines solvent extraction with the ring oven technique. Matic (32) has developed a procedure for the routine analysis of technical uranium solutions. He analyzed solutions from 17 uranium producing mines for the presence of 28 elements by this method.

(2) Anions: In 1961, Weisz (52) mentioned some 23 identification reactions for anions in his monograph. Since then, very few further applications have been made. Musil, Haas and Drabner (36) have reported a separation scheme for 8 common anions (bromide, iodide, thiocyanate, sulphate, chromate, phosphate, arsenate and hexacyanoferrate (II)) contained in a single drop of solution. Another systematic scheme for the analysis of common anions has been worked out by Biswas, Munshi and Dey (2). Mooney has developed an exclusion system by which 12 anions can be identified by employing a number of single tests performed in certain sequence. Separation of these anions is not necessary in such a procedure. Ions identified in this scheme are nitrate, borate, silicate, phosphate, sulphate, molybdate, fluoride, cyanide, chromate, bromide, iodide and chloride.
C. QUANTITATIVE DETERMINATION

Spot colorimetry is a promising quantitative analytical method. Ring oven methods are not different from spot colorimetry in principle. However, they are more sensitive because the constituents of the spot are concentrated into a ring of much smaller area as compared to that of the spot. Analysis at submicrogram levels can easily be performed by means of ring oven and quantitative results are obtained quickly, easily and very clearly.

In this type of analysis, rings of unknown concentrations are visually matched against the rings of standard concentrations. Ottendorfer (37) compared the visual measurements of the rings against instrumental density measurements. He found that mere visual comparison of the rings is at least equal if not superior to the instrumental measurements.

Often, several procedures can be developed for the determination of any particular ion by choosing a suitable chemical reaction and separation or masking procedure. This choice, of course, depends upon the type of interfering ions likely to be present in the sample and the sensitivity required.

D. TRACE ANALYSIS

Feigl and West (14) in 1957 pointed out the possibility of using the ring oven in trace analysis. Since then, this simple technique is becoming more and more popular. Already about 75 papers have appeared dealing with trace analyses by the ring oven technique.
E. AIR POLLUTION STUDIES

Ring oven methods can be very useful for air pollution studies. The analysis of airborne particulates and aerosols is one of the most important problems of chemical analysis. It is very important to control the impurities in air for public health and hygiene.

Although relatively large amounts of sample can be collected by the use of high volume samplers over an extended period of time, it is more desirable to collect smaller samples during brief sampling periods, if methods for analysis of these small samples are available. Such methods should be capable of isolating, concentrating, identifying and determining small quantities of various materials present in the air. The ring oven technique in conjunction with several sensitive chemical reactions, now well known, fulfills these conditions and can therefore be used in this field with advantage.

Methods for the estimation of antimony (56), beryllium (57), selenium (54), caffeine (59), and sulfate (22), in air have been worked out.

F. RADIOACTIVE SUBSTANCES

The ring oven also provides a simpler approach for the determination of radioactive material. A simple procedure for such analysis is as follows:

A standard scale is prepared by making rings of 1, 2, 4, 6, 8, 10 and 15 microliters of standard solution of the radioactive substance. These rings are exposed to X-ray film for certain known periods of time and the corresponding rings are developed on the film. Then, three similar autoradiographs are prepared under similar conditions.
with different but known volumes of sample solution. These unknown rings are matched with rings of the standard scale. Concentration of the unknown solution can easily be calculated from the known concentration of the matching rings. This method gives good results but it is time consuming.
A. INTRODUCTION

If the total quantity of sample material available is very small, spectrographic and neutron activation procedures are the only ones of the various procedures discussed in Chapter II that would be capable of determining trace quantities of vanadium present. Both of these techniques require very expensive equipment and highly trained personnel. The ring oven technique, as already discussed, provides a sensitive means for the determination of metals such as vanadium. As little as 0.1µg of vanadium present in a microliter of solution can be determined.

West and Conrad (55) reported a selective spot test for the detection of vanadium. They found that a yellow precipitate is formed between α-Benzoinoxime and vanadate ion in acidic solution. Probably there is anhydride formation between the -OH groups of the metalloacid and -OH or -NOH group of the benzoinoxime molecule.
This reaction has been used to develop a procedure for the determination of vanadium (V). The selectivity of this procedure is further enhanced by extracting the yellow precipitate with benzene and the sensitivity is increased by concentrating the product into a ring.

B. EXPERIMENTAL

Reagents: α-Benzoinoxime; saturated solution in ethanol.

Benzene.

Standard vanadate solution; prepared by dissolving 0.2298 g of pure dry ammonium metavanadate in 3N sulfuric acid such that the final volume of solution be 1 liter. Solution contains 0.1μg of vanadium per microliter.

Apparatus: Weisz ring oven with accessories (National Appliance Co.)

Surface thermometer (Pacific Transducer Corp., Model 311F.)

Hair drier.

Lambda pipets and solvent pipets.

Schleicher and Schuell filter paper No. 595 of 5.5 cm diameter.

C. PROCEDURE FOR PREPARING RINGS

Place a filter paper, the center of which has been previously marked with a sharp pencil or a pin, on a ring oven maintained at about 100°C. The temperature of the ring oven can be easily adjusted by means of a powerstat and measured with a surface thermometer.
placed on the hot surface of the ring. Two microliters of a saturated solution of α-benzoinoxime in ethanol is placed on the center of the filter paper by means of a lambda pipet passing through the guide tube of the ring oven as shown in Figure 11. After placing α-benzoinoxime at the center, one or more μls of solution containing vanadium (V) is slowly added to the center of the filter paper. A very faint yellow spot may appear at the center. The spot at the center is thoroughly washed with benzene which is added by means of a solvent pipet passing through the guide tube. The rate of addition of benzene is so adjusted that it evaporates as soon as it reaches the edge of the ring zone. If the rate of addition is very slow, benzene will evaporate before reaching the edge of the ring oven and the ring obtained will be diffused. Also, if the rate of addition of benzene is too rapid, the benzene will pass over the edge and evaporate quickly on the hot surface, thus, resulting in a diffused ring. The time sequence of successive washings can be easily adjusted with very little practice. As benzene spreads on the paper it dissolves the yellow compound formed between vanadium(V) and α-benzoinoxime. When the benzene solution reaches the hot circular edge of the ring zone, the solvent evaporates leaving behind a yellow ring. The intensity of the color of the ring is proportional to the concentration of vanadium present in the solution.

D. ANALYSIS OF AN UNKNOWN

The general procedure described earlier is followed for the preparation of each ring. The standard scale is conveniently prepared by making rings with 0, 1, 2, 4, 8 and 10 μl drops of solution
Figure 11
THE RING OVEN
containing 0.1μg/μl of vanadium (V). In each case, two microliters of α-benzoinoxime solution is used. The product is stable and the rings of standard scale can be stored for a number of days for comparison with those of unknown concentration. For the best results, the unknown solution containing vanadium (V) should be 3N with respect to sulfuric acid. A ring is made from 1 μl of unknown solution vanadium (V) and matched with the standard scale.

In general, when a ring is made from one drop of unknown solution and compared with the standard scale, three possibilities can arise:

1. The ring is less intense than standard ring of 1 μl; hence the unknown solution is weaker than the standard solution and the ring must be made with larger volume of unknown solution, say 5, 6, 10 μls or even more.

2. The ring is more intense than the standard ring of 10 μls; in such a case the concentration of the unknown solution is more than ten times that of the standard solution and the unknown solution should be diluted such that the unknown rings fall within the range of scale.

3. The ring fits into the scale; in such a case the ring is matched on the scale and an estimate can be easily made about the concentration of the unknown solution.

For more accurate analysis the following procedure is recommended.

Let the rings of standard scale be numbered I, II, III, --X, etc. according to the increasing amount of vanadium present in the rings.

Now make three rings with different numbers of microliter portions of
the unknown solution, say 1, 2 and 3 µls of the solution such that the intensity of these rings falls within the range of the standard scale. For example, unknown ring with 1 µl may match with ring II of the standard scale and unknown rings with 2 and 3 µls may match with rings V and VI, respectively.

TABLE XI
DETERMINATION OF THE CONCENTRATION OF UNKNOWN SOLUTIONS

<table>
<thead>
<tr>
<th>Volume of Unknown Solution (µl)</th>
<th>Matching Ring on Standard Scale</th>
<th>Amount of Vanadium in Standard Ring (µg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>II</td>
<td>0.2</td>
</tr>
<tr>
<td>2</td>
<td>V</td>
<td>0.5</td>
</tr>
<tr>
<td>3</td>
<td>VI</td>
<td>0.6</td>
</tr>
<tr>
<td>TOTAL</td>
<td>6</td>
<td>1.3</td>
</tr>
</tbody>
</table>

Concentration of the unknown solution = 1.3/6 = 0.22 µg/µl.

E. RESULTS AND DISCUSSION

Accuracy and reproducibility of the method for microdetermination of vanadium were ascertained by the procedure described above. Results are shown in TABLE XII.
TABLE XII

DETERMINATION OF VANADIUM

<table>
<thead>
<tr>
<th>Taken (μg)</th>
<th>Found$^a$ (μg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>0.308 ± 0.013$^b$</td>
</tr>
<tr>
<td>0.5</td>
<td>0.494 ± 0.011</td>
</tr>
</tbody>
</table>

a. Based on averaging 5 values calculated from three rings each.
b. Calculated at 90% confidence limit.

F. SELECTION OF FILTER PAPER

Many qualities of filter papers were examined, and those checked were found to be free of vanadium contamination. Because washing with organic solvents having low boiling points like benzene is very easy and does not effect the strength of the paper, most filter papers were found to be suitable. In the present investigation, however, Schleicher and Schuell No. 595 filter paper of 5.5 cm diameter was used.
G. STUDY OF INTERFERENCES

The interference effects of the following ions were examined:

Group I. Li⁺, Na⁺, K⁺, Cu⁺², Rb⁺, Ag⁺, Cs⁺ and Au⁺³.
Group II. Be⁺², Mg⁺², Zn⁺², Sr⁺², Ca⁺², Cd⁺², Ba⁺² and Hg⁺².
Group III. Al⁺³, Ga⁺³, Ce⁺⁴ and Tl⁺.
Group IV. SiO₃⁻², Ti⁺⁴, GeO₃⁻², Zr⁺⁴, Sn⁺⁴, Pb⁺² and Th⁺⁴.
Group V. NH₄⁺, NO₃⁻, HPO₄⁻², As⁺⁵, Sb⁺⁵ and Bi⁺³.
Group VI. SO₄⁻², CrO₄⁻², SeO₄⁻², MoO₄⁻², TeO₄⁻² and WO₄⁻².
Group VII. Cl⁻, ClO₄⁻, Mn⁺², Br⁻, BrO₃⁻, and I⁰⁻.
Group VIII. Fe⁺³, Co⁺², Ni⁺² and Pt⁺⁴.

H. METHOD OF TESTING INTERFERENCES

The effect of interfering ions was investigated by preparing two rings for each ion. One ring contained 10 g of interfering ion and the other ring was prepared with 1 µl of solution containing 0.5 µg of vanadium and 10 µg of interfering ion. These two rings were matched with blank and standard ring (containing 0.5 µg of vanadium) respectively.

I. RESULTS OF INTERFERENCE STUDY

Among the ions tested only Fe⁺³ slightly intensifies the yellow color of the ring. This interference was easily overcome by adding a few drops of 3N H₃PO₄ to the unknown solution until the pale yellow color, due to iron, disappeared. Acidity of unknown solutions is an important factor. If the solution is not properly acidic, i.e. 3N with respect to H₂SO₄, copper ions may interfere with the test.
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VITA

Sham Lal Sachdev was born at Hoshiarpur, India, on December 21, 1937. He graduated from D.A.V. High School at Hoshiarpur in April, 1954. He then joined Panjab University at Chandigarh, India and received a B.S.(Hons.) and M.S. in the years 1959 and 1960, respectively. From October, 1960 to August, 1961, he worked as a chemistry teacher at D.A.V. College Chandigarh. In September 1961, he entered the graduate school of Louisiana State University, Baton Rouge, and is presently a candidate for the degree of Doctor of Philosophy in chemistry.
EXAMINATION AND THESIS REPORT

Candidate: Sham Lal Sachdev

Major Field: Chemistry

Title of Thesis: New Methods for the Determination of Trace Quantities of Vanadium

Approved:

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Major Professor and Chairman

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Dean of the Graduate School

EXAMINING COMMITTEE:

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Date of Examination:

Friday, December 17, 1965