REDOX REACTIONS

ON

THE RING OVEN

BY

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This work is dedicated to my children Mary and Joseph.

ABSTRACT

The ring oven is used for the microdetermination of mercury (I and II) and silver. Very few ions interfere and these are of no significance in air and water pollution work.

The methods proposed are based on a novel application of the ring oven. Instead of precipitating mercury and silver with conventional reagents, these ions are reduced to the metallic condition on the ring and their determination is made by measuring the intensities of the rings formed. 0.5 µg. of mercury (I and II) and 0.05 µg. of silver can thus be determined.

A new Schiff base is proposed for the specific and sensitive detection of cadmium without prior separation. The limit of identification is 0.025 µg. of cadmium.

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PART ONE

I. INTRODUCTION

The ring oven technique has recently been used for the microdetermination of a number of inorganic and organic materials[1]. The technique which was developed by Dr. H. Weisz at the Institute for Analytical Chemistry in Vienna in 1954 has now gained wide recognition and is used in many fields of analytical chemistry. First designed as a technique which permits the identification of a large number of ions in a microdrop, the method quickly developed into a quantitative method for determining organic and inorganic materials. The potential applications of the method whether for qualitative analysis, quantitative analysis, radiochemistry etc. seem excellent. The different possibilities of the ring oven are exhaustively discussed by Weisz[2]. In the methods hitherto reported, the determinations were made by washing the reaction product to the ring or by carrying the reaction on the ring. In the methods proposed in this thesis, the material is brought to the ring where it undergoes reduction reactions and is thus determined by the intensity of the reduced product. The methods have proved to be simple, fast and specific. No special reagent or training are required. The methods proposed are particularly suitable for air pollution work and, with appropriate modifications, can be applied for the microdetermination of other materials by redox reactions.

Part I of this thesis covers the microdetermination of mercury and silver by the ring oven technique. Mercury is determined by reducing it to the metallic condition using hydroxylamine hydrochloride, while silver is revealed by means of a photographic developer. The limits of identification are 0.5 µg. and 0.05 µg. while the range for determination are 1 to 10 µg. and 0.1 to 0.7 µg. for mercury and silver respectively.

Part II describes a new spot test for cadmium using the Schiff base 2,2'_(2,6-pyridinediylbis methylidynenitrilo) diphenol. A procedure is described for the specific and sensitive detection of cadmium in the presence of as many as 38 cations. Specificity is achieved by masking, pH control and solvent extraction, with a limit of detection of 0.025 µg. of cadmium.

II. GENERAL PRINCIPLES OF THE RING OVEN

Separation of the components of a sample is one of the most important steps in the process of the qualitative and quantitative analysis of these components. If the volume of the sample available is very small (e.g. 1 μliter), such separation would be impossible by the usual methods of filtration and centrifugation. It is possible however, to place a drop of the sample (in a solution form) on a filter paper, thus letting the solution seep in the pores of the paper. If a reagent is added, which precipitates some of the components of the sample, a precipitate is formed at certain localities, and the solution carrying the unprecipitated constituents moves towards the edges of the paper.

This is the basis of the Weisz ring oven technique originally demonstrated by Weisz around 1954[3]. Shortly after its introduction, the ring oven found wide application in various branches of analytical chemistry. This was due to the advantages the new technique offered. Such advantages include:

1.- Simplicity and speed.

2.- No elaborate apparatus is required.

3.- Identification of several ions in a microdrop of sample solution.

4.- Quantitative determinations through the concentration of substances in the form of sharp, well-defined rings. These rings can be regarded as "circular spots". This type of

analysis, usually referred to as "ring colorimetry" is much more accurate than spot colorimetry. The latter usually involves excessive errors due to inhomogeneity of spots and inaccurate color matching.

5.- Combination of the ring oven with other techniques such as electrography, autoradiography, paper chromatography etc.

III. DESCRIPTION AND MODE OF OPERATION OF THE RING OVEN

The ring oven is shown in Fig. 1. It consists of a cylindrical block of aluminium, 35 mm. high and 55 mm. diameter, with a central bore-hole of 22 mm. diameter. The block is heated by a heating element controlled by a powerstat. The operating temperature should be in the range of 125° to 150°C when aquous solutions are used, lower temperatures being required with low boiling solvents. A ring, which has an outside diameter about the same as the heating ring, but an inside diameter 4-5 mm. greater than the inside ring of the heating block is provided to hold the filter paper firmly against the hot surface. Capillary pipets can be inserted in a guide and are thus centered on the filter paper. A small electric lamp situated at the base of the ring oven below the heating block allows the edge of the oven to be seen and so enables the elution to be controlled more precisely.

Mode of Operation of The Ring Oven:

A drop of standard or unknown solution is placed in the center of a round suitable filter paper which is placed on the hot ring oven so that the spot of solution lies centrally just underneath the guide tube. The filter paper is kept in place by the means of/metallic ring holder. The solution is then washed out with a solvent by means of a capillary pipette. This pipette is filled simply by touching it to the surface of the solvent, and is then placed upon the solution spot through the guiding tube. The filter paper absorbs the solvent and the solution migrates. The wet spot

Fig. 1. The ring oven.

spreads concentrically and the pipette is refilled and again placed on the spot.

When the liquid reaches the edge of the bore-hole of the hot block, the solvent vaporizes, hence the size of the wet spot can never exceed the diameter of the bore hole (22 mm.). The dissolved components are transported to this point where they remain as a sharply defined ring zone. The flow of solvent from the pipette need not be regulated because the volume of the pipette is very small (the inner diameter of the capillary is about 0.1 mm.) and because only as much liquid can leave the pipette as the paper can absorb. The entire procedure takes only a few minutes.

The actual area of the ring, which is as thin as a pencil line, is quite small. Even if the width of the ring were 1 mm., the area of the ring would be less than 70 mm^2. i.e.

$$2 \pi r \times \text{width} = 22 \times 3.14 \times 1 = 69.1 \text{ mm}^2.$$

The ring is therefore smaller than a spot of 10 mm. diameter which corresponds to a drop volume of about 1.5 µl. i.e.

$$\pi r^2 = 25 \times 3.14 = 78.50 \text{ mm}^2.$$

However, with the concentrations normally used in microchemical work the ring zone is generally narrower, i.e. 0.1 - 0.3 mm., so that the area of the ring zone is even smaller, or about 7 - 20 mm^2.

Thus the actual concentrations of the eluted substances in the ring zone are three to ten times greater than in the original spot.

The ring oven technique has been successfully used for the qualitative identification of a large number of ions in a microdrop.

Weisz[4] described a method whereby the mixture is washed to the ring, the filter paper is then cut in small sections, each being used for the identification of a cation.

West and Mukherji[5] described a scheme for the separation and identification of 35 metallic ions in a single drop, based on solvent extraction. Complete separation and identification can be made in an hour.

Quantitative determinations are readily made by the ring oven technique; materials that have been quantitatively determined include caffeine, phosphate, nitrate, copper, beryllium, selenium, zinc, antimony. Procedures for the quantitative estimations of the rings are described later.

IV. HISTORICAL

A. Methods For Determining Mercury

Essentially the methods hitherto applied for the determination of mercury are:

Gravimetric, potentiometric, chromopotentiometric, amperometric, complexometric, spectrophotometric, spectrographic, paper chromatography, neutron activation, X-ray fluorescence, and radiochemical.

Most of these methods involve lengthy and tedious operations; especially the gravimetric procedures which involve precipitation, filtration, washing and drying of the precipitate.

Mercury has been determined by precipitation as the sulfide by the addition of 1-amidino-2-thiourea at a pH greater than 10.5. Metals which interfere are complexed with EDTA, citric acid or cyanide. The accuracy is 2%[6].

Twenty milligrams of mercury could be determined with an error ±0.3% by precipitation as $Hg(C_{10}H_6NO_2)_2$ by the addition of α-nitroso-β-naphthol at pH 1.9[7]. Also 10.8 - 16.2 mg. mercury (II) have been determined by precipitating mercury as $Hg(C_{13}H_{10}NO_2)_2$ by N-benzoyl-N-phenylhydroxylamine (in ETOH) at pH about 4[8]. Interference of bismuth (III), arsenic (V), antimony (III) or tungsten (VI) is overcome by masking with sodium potassium tartrate; sodium-citrate masks the interference of these ions: cobalt (II), nickel (II), cadmium (II), lead (II), and silver (I). Sodium oxalate masks tin (IV), and sodium fluoride masks indium (III). Molybdenum (VI) which interferes with

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mercury (II) is separated by prior precipitation with 1% solution of the reagent in 1 N acid solution. Chloride, cyanide, and disodium EDTA interfere.

Thiourea is used to determine mercury since mercury (II) and thiourea form a white precipitate of $Hg(HNCSNH_2)_2$ at pH 4.4 - 6.8[9], but it also forms other double salt at pH $>$ 7.2. Therefore the reaction is not recommended for determination of mercury (II) especially at pH $>$ 7.2.

Fifty to five hundred µg. of mercury can be determined by the cyanogen bromide method[10]. In this method mercury (II) is reacted with potassium cyanide, the excess cyanide ions bound by formaldehyde, and the mercury (II) cyanide converted to cyanogen bromide by bromine water. The cyanogen bromide is determined iodometrically. Silver (I), copper, and iodine interfere.

A range of 90 - 268 mg. mercury (II) has been determined with a mean error of 0.2% and mean deviation of 0.04 by the selective quantitative displacement of mercury (II) from an EDTA - Hg complex by sodium thiosulfate solution[11].

Potentiometrically, mercury has been determined with iodine (I) chloride[12]. A platinum electrode is used as indicator and a saturated calomel electrode as reference. The mean error for the determination is 0.7% for a solution containing 170 mg. mercury.

A similar potentiometric titration with 0.1 N iron (III), is used to determine down to 5 mg. of mercury (II) in 50 ml. with a 1% relative error[13].

Small quantities of heavy metals are determined chronopotentiometrically in the presence of large amounts of metals with low standard potential[14]. Concentrations of 10^{-5} - 10^{-8} mole/ml. mercury are determined with an accuracy of ±5%.

Amperometrically, mercury is determined in ores containing $\leqq$ 0.5% copper, $\leqq$ 2.0% zinc, $\leqq$ 0.4% lead and $\leqq$ 12% iron by titration with unithiol[h] at 0.6 - 0.8 v.[15]. Iron is masked with ammonium fluoride or sodium perphosphate. Sensitivity of the method is 2 µg. mercury/ml.

The tendency of mercury(II) ions to form water-soluble undissociated mercury(II) cyanide is so great that they can liberate iron(II) ions from ferrocyanide ions. If this demasking occurs in the presence of α- α′-dipyridyl, a red color appears because of the formation of $\boxed{Fe(\alpha,\alpha'\text{-dip.})_3}^{++}$ ions. This has been applied as a test for the determination of mercury[16]. Silver(I) and palladium(II) ions interfere. The limit of identification is 2 µg. mercury.

1-phenylthiosemicarbazide is a strong reducing agent for mercury(I) in neutral and acid media. The reduction products (elemental metals) have distinct colors and can be detected in small quantities. Sensitivity for mercury(I) is 0.65 µg./µl.[17]

Mercury is also determined to a sensitivity of 2 µg. with papaverine potassium iodide reagent which forms a white precipitate with mercury[18]. Interference of iron(III), cobalt(II), silver(I), lead(II), copper(II), and bismuth(III) is eliminated by addition of 1% phosphoric acid and interference by thiosulfate and sulfite ions by oxidation with bromine water.

To detect mercury(II) in solution, the rose white copper(I) iodide is added which, in presence of mercury(II) turns orange-red due to the formation of mercury(II) iodide[19]. Sensitivity is 10 µg./ml.

Mercury(II) forms with dithizone a yellow green complex, soluble in carbon tetrachloride[20]. This was used to determine 10^{-4}% mercury.

The displacement of nickel from chloroform solution of its antipyrine-4-dithio carboxylate by mercury(II) ions is used to determine small amounts of the latter by observing the decrease in absorption at wavelength 575 mµ. Gold(I), mercury(I), copper(I), thiosulfate, sulfite, and cyanide ions and EDTA interfere with the determination[21].

B.I. Gurnits and G.P. Chuklenkova[22] describe/a determination of mercury vapor in the air of industrial areas. One method involves the use of an indicator tube with a colored column from which the mercury vapor concentration is read directly from the height of the column in the tube. In another method they use an indicator powder in chromatography tubes packed with silica gel. The principle used for both methods is the formation of a double mercury iodide salt having a yellowish rose color. The first method is more accurate and is recommended for use. Sensitivity is 0.01 mg./cu.m.air. Time for one determination is 5 - 20 minutes.

C.H. James and J.S. Webb[23] made a sensitive mercury vapor meter for use in geochemical prospecting. The instrument is specific for mercury with a sensitivity, of 10^{-4} µg. Two photocells receive the

light from a fused silica low pressure mercury vapor lamp . The lamp radiates mostly at 2537 A. at which frequency mercury shows the strongest absorption.

V.D. Yablochkin[24] tested for mercury in biological materials by immersing oxide-free copper spirals in a suspension of the sample in hydrochloric acid for 24 hours, washing, drying, exposing to bromine vapors for 30 seconds, and inspecting under UV light. If the mercury concentration is more than 1:20000, a red luminescence appears.

Rudolf Hradcorsky[25] determined mercury vapors by passing them in vaccuo over pure zinc. The amount of diffused contaminants is determined by spectral analysis or luminescent methods. The sensitivity is 10^{-2}% and the error is 10^{-6}%.

Mercury is determined by ultraviolet spectrophotometric method with EDTA (H_4L) and thiocyanate ions by measuring the absorbance of $HgL(SCN)^{-3}$ at 235 mμ against a reagent blank. An amount of 0.08 - 1.40 mg. of mercury can be determined by this method[26]. Cyanide, copper(II), vanadate ions, cobalt(II), molybdenum(VI), and silver(I) ions interfere very seriously.

Mercury(II) forms a 1:1 complex with cresophthalein at pH 9.6 - 10.3[27]. The complex obeys Beer's law at 583 mμ for the range 5 - 200 μg. mercury 150 ml. cyanide, iodide, sulfide, cadmium(II), copper(II), calcium(II), magnesium(II), nickel(II), silver(I), manganese(II), zinc(II), aluminium(III), lead(II) and cobalt(II) ions interfere.

The 1:1 complex of mercury and 1-(2-pyridylazo)-2 naphthol is

extracted with chloroform at pH 7.5 - 11.5. The complex absorbs at 555 mμ. Beer's law is followed for 0.50 μg. of mercury per 10 ml. of chloroform. Copper, zinc, nickel, cobalt, iron(III), manganese, arsenic(V), and antimony(III) interfere but mercury can be separated by distillation[28].

I.F. Marozova and V.A. Sal'manova[29] described a procedure for the quantitative spectrographic determination of small amounts of mercury in mineral raw materials. The determinable concentrations are 0.0002 - 0.01% for a 150 mg. sample and 0.001 - 0.01% for a 50 - 150 mg. sample.

Mercury in biological material has been detected by paper chromatography[30]. The solution, after mineralization with sulfuric-nitric acids is distilled, the distillate neutralized to pH 7, centrifuged and the supernatant chromatographed with methyl acetate-methyl alcohol-water (87:3:10). The spots are located by color reaction with diphenyl carbazone. The limit of detection is 1 μg.

Mercury is determined in air by atomic absorption spectrometry when the samples from the atmosphere are directly supplied to the burner of the spectrophotometer. The limit of determination is $\geq 10^{-6}$ g. mercury/m^3. in air by using mercury vapor lamps emitting at 2537 A.[31]

Several procedures are described for the determination of mercury by neutron activation. J. Pauly and G. Guzzi[32] developed a computer method in order to derive from γ-ray spectrum of a neutron activated material the detection limits for a great number of trace elements. A sensitivity spectrum is calculated from experimental data. The

detection limit for 57 elements is then deduced by using library data of special activities.

E.M. Lobanov[33] determined mercury in ores and concentrates by neutron activation. The sensitivity is about 0.1% mercury and the average relative precision is 10%.

Pierre Martinelli[34] determined the percentage of mercury in a sample by means of γ-radiation emitted by a radioactive isotope such as iridium 192 which has several times the energy of the fluorescent K-ray of mercury.

X-ray fluorescence methods were applied to the determination of trace toxic elements in water[35]. Concentrations as low as 0.01 p.p.m. can be determined.

Radiochemical determination of metallic mercury vapor in air was tried by L. Magos[36]. Passage of mercury contaminated air through a solution of $Hg^{203}(OAc)_2$-KCl results in isotope exchange causing the effluent air to contain mercury in the same concentration as in the influent air and in the same special activity as in the solution. The mercury 203 is absorbed on hop-calite and established by γ-scintillation counting.

A critical review of these methods shows that for mercury, sensitivity is often achieved at the expense of specificity. Further a number of these methods are quite elaborate, time consuming and require specialized equipment. Hence the need for a method which is simple, fast, specific; and which could be used for air pollution work.

B. Methods for Determining Silver

Methods similar to those used for the determination of mercury have been applied for the determination of silver. These methods are: gravimetric, atomic absorption, spectrophotometric, colorimetric, paper chromatography, potentiometric, electrodeposition and subsequent neutron activation, polarographic, and radioactivation.

B.C. Bera and M.M. Chakrabarthy[37] determined silver by precipitating it as $C_8H_7N_2SAg$ with 2-methyl mercaptobenzinidazole at pH 8.6 - 10. Mercury(I) interferes unless oxidized to mercury(II).

Silver is also precipitated with diazoaminobenzene I as AgI_2OH, then the precipitate is calcined quickly to silver. The error increases from ±0.3% for 34 - 113 mg. to ±1.5% for 2 - 22 mg. silver[38].

A method has been proposed for the gravimetric determination of traces of silver. The filter paper is uniformly impregnated with silver chloride solution, then the unknown silver solution is applied to the paper, followed by potassium cyanide. Silver is determined by comparing the weight of the paper with the weight of another paper containing a known concentration of silver. This method permits the determination of 16 - 30 μg. silver with an accuracy of ±1.5%. Iodide ions and iodine interfere[39].

Ling[40] determined silver on photographic films by atomic absorption spectrophotometry. A minimum of 6.5 μg. silver is needed per sample for optinum measurement, and 0.1 μg. 1 cm^2 can be detected.

The coefficient of variation is 1.6%.

One to nine thousand parts per million of silver in mineralized rocks can be determined by dissolving the material in nitric acid and atomizing it into the flame of an atomic absorption spectrophotometer. The atomic absorption is measured at 3284 A[41].

Trace amounts of silver(I) were determined spectrophotometrically as the 2-amino-6 methyl thio-4-pyrimidine carboxylic acid chelate[42]. The absorbance is measured at 375 mμ. Arsenic(III), chromium(VI), bismuth(III), iron(III), gold(III), selenium(IV), zinc(III), copper(II), thallium(III), and cobalt(II) destroy the chelate to some degree; arsenic(V), lead(II), nickel(II), strontium(II), barium(II), lanthanum(III), iridium(III), manganese(II), magnesium(II), cadmium(II), yttrium(III), cerium(IV), thorium(IV), titanium(IV), cobalt(II), iron(II), calcium(II), and cerium(III) also form insoluble precipitates which adsorb the chelate to some degree; interference is also caused by periodate and bromate ions.

Fourteenth μg./ml. of silver can be determined colorimetrically at 400 mμ by using 1-amidino-2-thiourea as the reagent with an accuracy of 3.5%[43]. In a concentration range of 1 - 12 μg./ml. Beer's law is obeyed. Mercury(II) and gold(III) interfere.

By measuring the absorbance of a solution of the silver enoldithizonate in carbon tetrachloride 1 μg. silver can be determined[44].

A procedure for the colorimetric determination of silver (2-100 μg.) consists in adding nitric acid, mercury(II) nitrate, ammonium persulfate, copper(II) sulfate, dimethylglyoxine and pyridine

in certain concentrations to the sample solution. The rose color of the mixture obtained is compared with a series of standard solutions. The error is ±5%[45].

Silver is detected by applying it on arsenic(III) sulfide paper and warming the paper; a black-brown stain or ring of silver(I) sulfide is formed. The limit of identification is 1 µg. silver[46].

The determination of silver by paper chromatography is based on the reaction of silver(I) with zinc(II) sulfide or copper(II) ferrocyanide when insoluble silver compounds are formed. Sensitivity is 32 µg. silver(I). The error is ±1.7%[47].

Pyrolytic graphite electrodes are used to electrolyze, at 1.6 v vs SCE, 10^{-5} M solution of silver(I). The resulting film is irradiated in the thermal neutron flux of a nuclear reactor. This technique is used for the quantitative determination of silver deposited from 10^{-5}, 10^{-6}, and 10^{-7} M solutions[48].

A polarographic method was developed for the determination of silver employing the principle of electrochemical masking for eliminating interferences by some frequently associated metals. Camphor was used as the masking agent. Gold and thorium interfere[49].

Silver as well as antimony and cerium are determined simultaneously by radioactivation of the elements to long-lived radionuclides[50]. The samples are activated 28 days in a flux of about 1.5×10^{12} neutrons/cm^2. sec. Sensitivity is about 0.01 - 0.5 p.p.m. silver.

Recently J.J. Janjic, G. Jurisic and M.B. Celap[51] determined

silver(I) and mercury(II) with the ring oven technique. These ions were reduced at the ring using formic acid and sodium formate; sensitivities are 5.3 to 7.9 µg. for silver and 2 to 6 µg. for mercury. The work described in this thesis was initiated before Janjic et al. published their paper. The methods proposed here are appreciably faster, simpler and more sensitive, further silver is revealed by a photographic developer thus permitting lower limits of determinations.

A review of these methods shows that there exists a need for a direct simple method of estimating small quantities of silver particularly in view of the importance of this ion in water treatment problems.

V. EXPERIMENTAL

A. Determination of Mercury

1.- Reagents and Stock Solutions:

Hydrochloric acid 0.05 N.

Hydroxylamine hydrochloride 1% solution.

Stannous chloride 1% solution containing 1 ml. HCl conc.

Concentrated ammonium hydroxide.

Standard stock mercury solution: A solution containing 10.00 µg. mercury per µl. was prepared by dissolving 1 g. of pure mercury in a few drops of concentrated nitric acid, boiling gently to expel brown fumes and making up to 100 ml. with distilled water. The standard stock solution was diluted as necessary for preparing standard working solutions.

Apparatus:

Weisz ring oven with accessories, National Appliance Co., Portland, Oregon.

Powerstat, Superior Electric Co., Bristol, Connecticut, Type 116.

Calibrated Lambda pipettes.

Whatman filter paper No. 2.

2.- Procedure:

Place the filter paper on the heated ring oven with the powerstat maintained at reading 28. Add

the appropriate volume of the mercury standard or unknown solution, followed by two 10 µl. portions of hydrochloric acid and two 10 µl. portions of hydroxylamine hydrochloride again followed by two 10 µl. portions of hydrochloric acid. After the transfer to the ring zone has been completed and the paper is about dry, remove it and expose it to the fumes of a hot concentrated ammonium hydroxide solution. A ring is formed.

3.- Rings with Foreign Ions

Table 1 shows the colors of rings obtained when 100 µg. of different cations were used.

Table 1

Colors Obtained with Various Cations

Cations	Color obtained	Cations	Color obtained
Sb(III)	colorless	Ni(II)	blue
As(III)	colorless	Au(III)	black
As(V)	colorless	Ag(I)	black
Bi(III)	colorless	Pd(II)	black
Ce(IV)	faint yellow	Cs(III)	colorless
Cr(III)	green	Rb(I)	colorless
Co(II)	dark brown	Th(IV)	colorless
Cu(II)	blue	Mn(II)	brown
Pb(II)	colorless	Pt(IV)	yellow
Al(III)	colorless	Ba(II)	colorless

Cations	Color obtained	Cations	Color obtained
Be(II)	colorless	Hg(I)	black
Cd(II)	colorless	Hg(II)	black
Li(I)	colorless	Mg(II)	colorless
K(I)	colorless	Sr(II)	colorless
Na(I)	colorless	Zn(II)	colorless
Zr(IV)	colorless	NH_4(I)	colorless
Tl(I)	colorless	Sn(IV)	colorless
Rh(III)	yellow	Sn(II)	colorless

It is apparent, that a number of these ions interfere under these conditions of operation and concentration. The interference of silver, gold and palladium was expected. Various attempts were made to mask the interfering ions. Masking agents tested for masking ability included acetate, citrate, oxalate, malonate, phosphate, fluoride, EDTA. None of these could be used because they either reduced the sensitivity of the mercury test or prevented it completely.

Trials were then made to dip the rings obtained in various acids of different strength. This helped by dissolving the hydroxides; the mercury was however often washed also.

It was however found that a 1% solution of stannous chloride gave the best results in removing the effect of interfering ions while the mercury color seemed actually to deepen.

Table 2 shows the colors obtained when 100 µg. of different anions were used.

Table 2

Colors Obtained with Various Anions

Anions	Color obtained	Anions	Color obtained
CNS^-	colorless	$SO_4^=$	colorless
$S_2O_3^=$	colorless	Br^-	colorless
Cl^-	colorless	I^-	colorless
CN^-	paint black	ClO_4^-	colorless
$HPO_4^=$	colorless	$CrO_4^=$	yellow
$S^=$	colorless	$[Fe(CN)_6]^{4-}$	blue
$[Fe(CN)_6]^=$	green	$SO_3^=$	colorless
IO_4^-	colorless	F^-	colorless
$Cit.^{3-}$	colorless	$tart.^=$	colorless
$Mo_7O_{24}^{6-}$	blue	BrO_3^-	colorless
$S_2O_8^=$	colorless	IO_3^-	colorless
$B_4O_7^=$	colorless	$CO_3^=$	colorless
$TeO_3^=$	very faint black	$Cr_2O_7^=$	orange
$C_2O_4^=$	colorless	MnO_4^-	brown

The interference of anions is not significant since it appears with anions which do not normally occur with mercury.

4.- Choice of Filter Paper:

Various filter papers were tried and the results were as follows:

Munktells OOH,OO and O	gave very poor rings.
Munktells OK and OOR	gave poor rings.
Whatman No. 40	gave better rings than above.
Whatman No. 1 and 2	gave good rings.

This is in conformity with observations made by other workers namely that the choice of the proper filter paper is an important factor in the procedure.

It thus appears that the filter papers that give good results are Whatman No. 1 and 2. These are qualitative analysis filter papers that have not been washed with acids. Munktells No. OOH, OO,O, OOR, OK and Whatman No. 40 are all double acid washed with hydrochloric and hydrofluoric acids.

Evidently the fluoride and chloride ions are complexing the mercury and thus preventing its reduction at the ring. While no appreciable difference exists between Whatman No. 1 and No. 2 filter papers the latter was finally selected because it is heavier, has higher retention power and slower diffusion properties.

5.- Recommended Procedure:

After exposing the filter paper to hot concentrated ammonium hydroxide solution dip it in the stannous chloride solution for about 1 minute and then press it between two filter papers and allow to dry. Black rings, the intensities of which depend on the concentration of

mercury, will appear against the white background of the paper.

Running a blank i.e. carrying the above procedure without mercury leaves no ring whatsoever on the filter paper.

Using the above procedure it is possible to obtain faint rings of mercury corresponding to a concentration of 0.5 µg. mercury. It is however recommended that for quantitative determinations the range 1.0 µg. to 9 µg. be used, for beyond 10 µg. the rings becomes too dark and comparison between the intensities, difficult and subject to errors.

Both mercury(I) and mercury(II) can be determined by this procedure, the limits of determination being the same.

The average time required for obtaining the mercury rings is of the order of 1 - 2 minutes and the entire determination can be completed in less than 4 minutes, provided the standard is available.

6.- Analysis of an Unknown:

The preparations of rings for the standard scale and for an unknown follows the above procedure.

A standard scale is prepared by making rings with 1,3,5,7,9 portions of 10 µl. of a solution of mercury containing 0.1 µg. per µl. Three rings made from different numbers of microliter portions of the sample solution are sufficient for each unknown. The color of each of the 3 rings is matched with the standard scale and it is decided whether it matches one of the rings or it falls between 2 rings. The quotient obtained from dividing the total number of microliters of the 3 unknown rings, by the total microliters of the matching

standard ring, when multiplied by the concentration of the standard solution gives the concentration of the unknown[52].

7.- Interferences and Foreign Ions:

The effect of foreign ions was investigated by developing two rings for each species using the above procedure. The first ring contained 100 μg. of the foreign ion while in the second ring 100 μg. of the foreign ion and 1 μg. of mercury were present. No interference was recorded for all cases when the first ring gave a blank or gave a ring less intense than 0.5 μg. mercury, and the second matched a ring containing 1 μg. mercury when judged visually.

The possible interfering effects of the following ions were investigated:

Table 3

Ions Investigated in Mercury Determination

Group I.- Li(I), Na(I), K(I), Rb(I), Cs(I), Ag(I), and Au(III).

Group II.- Be(II), Mg(II), Ca(II), Sr(II), Ba(II), Zn(II), Cd(II), and Cu(II).

Group III.- Al(III), Ce(IV), Tl(I), and BO_2^-.

Group IV.- $CO_3^=$, acetate, oxalate, tartrate, citrate, Zr(IV), Sn(II), Sn(IV), Pb(II), Th(IV).

Group V.- NH_4(I), NO_3^-, $HPO_4^=$, VO_3^-, $HAsO_3^=$, $HAsO_4^=$, Sb(III), and Bi(III).

Group VI.- $S^=$, $SO_3^=$, $SO_4^=$, $S_2O_3^=$, $TeO_3^=$, Cr(III), $CrO_4^=$, $Cr_2O_7^=$, $MoO_4^=$, $WO_4^=$, and UO_2^{2+}.

Group VII.- F^-, Cl^-, ClO_3^-, ClO_4^-, Mn(II), MnO_4^-, Br^-, BrO_3^-, I^-, IO_3^-, CN^-, NCS^-, $[Fe(CN)_6]^{4-}$, and $[Fe(CN)_6]^{3-}$.

Group VIII.- Fe(III), Co(II), Ni(II), Rh(III), Pd(II), and Pt(IV).

Although tin alone does not interfere, 100 µg. of tin(II) interfere by preventing the reaction but when the concentration of tin is reduced to 10 µg. no interference is observed. When iron(III) is present in concentration of 100 µg., the filter paper must be dipped in 2% stannous chloride solution. Concentration of iron up to 50 µg. do not interfere. 10 µg. of silver(I) do not interfere but 50 µg. of silver interfere. Interference was however observed from Au(III), Pt(IV), Pd(II), Rh(III), $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$. These are of no practical significance in air pollution studies.

8.- Mixture of Mercury with Foreign Ions:

A mixture containing 20 µg. each of copper(II), nickel(II), iron(III), cobalt(II), chronium(III), and 1 µg. mercury(II) gave a ring for mercury that compared with the mercury ring alone.

9.- Accuracy and Reproducibility of Quantitative Estimations:

The accuracy and reproducibility of this method for the microdetermination of mercury was ascertained by the method of Weisz[52]. Standard scales covering the range 0.5 - 7 µg. mercury were prepared by the described procedure. Rings obtained from 10,30,50, and 70 µl. of an unknown were also developed and matched with standard rings. The ratio of the number of microliters of unknown to the number of microliters of standard is the concentration of the unknown solution referred to the standard solution. When this ratio is multiplied by the concentration of the standard (0.1 µg. of mercury per µl.) the

concentration of the unknown is obtained.

A typical calculation of statistical analysis for 1 µg. is shown below:

a.- Preparation of Standards:

4 rings S_1, S_3, S_5, and S_7 containing respectively 1 µg., 3 µg., 5 µg., and 7 µg. mercury(II) are prepared.

b.- Preparation of Rings:

5 rings I_1, I_2, I_3, I_4, and I_5 containing all of them 1 µg. mercury(II) are prepared.

5 rings I_1, I_2, I_3, I_4, and I_5 containing all of them 3 µg. mercury(II) are prepared.

Similarly rings containing 5 µg. and 7 µg. mercury(II) are prepared.

	I_1	I_2	I_3	I_4	I_5
S_1	matches	matches	matches	less than 1 µg. and darker than 0.5 µg. about 0.7 µg.	matches
S_3	matches	matches	4 µg.	matches	matches

The above values were arrived at by judging the intensity of the ring; when appreciably different, a complete unit was added or removed, when slightly different, 0.3 - 0.5 units was added or removed.

c.- Calculations for 1 µg.:

I_1	$\frac{50}{50} = 1$	1 x 0.1 = 0.1	0.1 x 10 µl. = 1 µg.
I_2	$\frac{50}{50} = 1$	1 x 0.1 = 0.1	0.1 x 10 µl. = 1 µg.

I_3	$\frac{50}{50} = 1$	1 x 0.1 = 0.1	0.1 x 10 µl. = 1 µg.
I_4	$\frac{50}{53} = 0.9434$	0.9434x0.1=0.09434	0.09434 x 10 µl. = 0.09434
I_5	$\frac{50}{50} = 1$	1 x 0.1 = 0.1	0.1 x 10 µl. = 1 µg.
			= 4.9434 µg.

Solution containing 0.1 µg./1 λ $\quad \bar{X} = 0.9887.$

d_1 =	1 - 0.9887 = 0.0113	d_1^2 = 0.00012769
d_2 =	1 - 0.9887 = 0.0113	d_2^2 = 0.00012769
d_3 =	1 - 0.9887 = 0.0113	d_3^2 = 0.00012769
d_4 =	0.9887 - 0.9434 = 0.0453	d_4^2 = 0.00204309
d_5 =	1 - 0.9887 = 0.0113	d_5^2 = 0.00012769
		$\sum d_n^2$ = 0.00255385

$$\sigma = \sqrt{\frac{\sum d_n^2}{n-1}} = \sqrt{\frac{0.00255385}{4}} = 2.53 \times 10^{-2}$$

t at 90% confidence limit = 2.13 for n = 5.

$$\mu = \bar{X} \pm t \frac{\sigma}{\sqrt{n}} = 0.989 \pm 2.13 \frac{2.53 \times 10^{-2}}{2.238} = 0.989 \pm 0.024.$$

Similar calculations are made for rings containing 3, 5 and 7 µg. mercury.

Results of analysis of two unknowns are given in table 4.

Table 4

Determination of Hg at 90% Confidence Limit

taken µg.	found (µg.)[a]
1 µg.	0.989 ± 0.024
3 µg.	3.043 ± 0.044

a) based on averaging 5 values calculated from 5 rings each.

10.- Discussion:

With the exception of the work of Janjic[51], quantitative determinations on the ring oven were made by washing the precipitate to the ring or forming a precipitate at the ring. In this method mercury is deposited in the free metallic condition by reduction with hydroxylamine hydrochloride. The choice of the reductant was dictated by redox potential considerations and in order to decrease the number of interfering ions. In acid solution (pH = 0) hydroxylamine hydrochloride has a formal potential of 0.7 v. while the potential for mercury(II)-mercury is 0.92 v. and the potential for mercury(I)-mercury is 0.79 v. It is therefore to be expected that palladium, platinum and gold with potentials of the order 0.99, 1.2 and 1.46 v. respectively and to a certain extent silver with a potential of 0.8 v. should interfere.

Presumably the mechanism of the reaction on the ring oven is the following: hydroxylamine hydrochloride first reduces mercury(II) to mercury(I). Mercurous chloride upon exposure to ammonia will form free mercury and basic mercury chloride.

$$Hg_2Cl_2 + 2NH_3 \longrightarrow HgNH_2Cl + Hg + NH_4^+ + Cl^-$$

The basic mercury salt is further reduced to metallic mercury by stannous chloride, which explains the fact that the color of the ring becomes more intense when the filter paper is dipped in it.

B. Determination of Silver

1.- Reagents and Stock Solutions:

Concentrated ammonium hydroxide.

Potassium bromide 0.05%.

Acetic acid 0.05 N.

Developer[53]: Potassium hydroxide 2.5 g.

Sodium sulfite anhydrous 20 g.

Potassium bromide 0.3 g.

Hydroquinone 5.5 g.

Distilled water up to 100 ml.

Fixer: Sodium hyposulfite 20 g.

Sodium bisulfite 2.5 g.

Distilled water up to 100 ml.

Standard stock silver solution: 1 g. of pure silver is dissolved in a few drops of nitric acid. The solution is gently heated to get rid of oxides of nitrogen and then diluted to 100 ml. with distilled water. The standard stock solution was diluted as necessary for preparing standard working solutions.

Apparatus:

Weisz ring oven with accessories, National Appliance Co., Portland, Oregon.

Powerstat, Superior Electric Co., Bristol, Connecticut, Type 116.

Calibrated Lambda pipettes.

Munktells filter paper No. OK.

2.- Procedure:

Place the filter paper on the ring oven with the powerstat maintained at reading 28. Add the appropriate volume of the standard silver solution or of unknown silver solution followed by four 10 µl. portions of concentrated ammonium hydroxide. Add one 10 µl. portion of potassium bromide solution followed by four 10 µl. portions of distilled water. After the transfer to the ring zone has been completed and the paper is almost dry, remove it and dip it in the developer for two minutes. Remove the filter paper from the developer wash it twice with distilled water and dip it in acetic acid solution for 10 minutes. Dip the filter paper in a beaker of distilled water and in the fixer solution and dry it using a stream of hot air. A black ring indicates silver.

Using the above procedure the limit of determination of silver is 0.05 µg. and the recommended range covers 0.1 - 0.7 µg. of silver.

The above procedure was applied to the ions tested in table 5, only silver, mercury and gold gave rings.

3.- Choice of Filter Paper:

Various filter papers were tried and the results were as follows:

Whatman No. 1 and 40	gave no rings.
Munktells No. OOR	gave poor rings.
Whatman No. 2	gave better rings than above.
Munktells No. OK, OO, OOH and O	gave good rings.

4.- Interferences and Foreign Ions:

The effect of interfering ions was investigated by preparing two rings for each ion. The first ring contained 10 μg. of the potential interfering ion and the second, 0.1 μg. of silver in presence of 10 μg. of interfering ion. No interference was recorded for all cases when the first ring gave a blank or gave a ring less intense than 0.05 μg. silver, and the second matched a ring containing 1 μg. silver when judged visually.

The possible interfering effects of the following ions were investigated:

Table 5

Ions Investigated in Silver Determination

Group I.-	Li(I), Na(I), K(I), Rb(I), Cs(I), Hg(I), and Au(III).
Group II.-	Be(II), Mg(II), Ca(II), Sr(II), Ba(II), Zn(II), Cd(II), and Cu(II).
Group III.-	Al(III), Ce(IV), Tl(I), and BO_2^-.
Group IV.-	$CO_3^=$, acetate, oxalate, tartrate, citrate, Zr(IV), Sn(II), Sn(IV), Pb(II), Th(IV).
Group V.-	NH_4(I), NO_3^-, $HPO_4^=$, VO_3^-, $HAsO_3^=$, $HAsO_4^=$, Sb(III), and Bi(III).
Group VI.-	$S^=$, $SO_3^=$, $SO_4^=$, $S_2O_3^=$, $TeO_3^=$, Cr(III), $CrO_4^=$, $Cr_2O_7^=$, $MoO_4^=$, $WO_4^=$, and UO_2^{2+}.
Group VII.-	F^-, Cl^-, ClO_3^-, ClO_4^-, Mn(II), MnO_4^-, Br^-, BrO_3^-, I^-, IO_3^-, CN^-, NCS^-, $[Fe(CN)_6]^{4-}$, and $[Fe(CN)_6]^{3-}$.
Group VIII.-	Fe(III), Co(II), Ni(II), Rh(III), Pd(II), and Pt(IV).

10 µg. of mercury(II) and mercury(I) interfered, but if the filter paper is dipped in a 10% sodium fluoride solution for 1 hour before it is dipped in acetic acid no interference is observed.

10 µg. of tin(II) interfered by preventing the formation of silver ring but if/the concentration is reduced to 1 µg. it will not interfere.

Gold(III) interfered.

5.- Accuracy and Reproducibility of Quantitative Estimations:

The accuracy and reproducibility of this method for the microdetermination of silver was ascertained by the method of Weisz[52]. Standard scales covering the range 0.05 µg. - 0.7 µg. of silver were prepared by the described procedure. The concentration of the unknown solution was determined in the same way as that used for mercury.

Results of analysis of two unknowns are given in table 6.

Table 6

Determination of Ag at 90% Confidence Limit

taken µg.	found (µg.)[a]
0.1 µg.	0.102 ± 0.0043
0.3 µg.	0.298 ± 0.0041

a) based on averaging 5 values calculated from 5 rings each.

PART TWO

SPOT TEST FOR CADMIUM

I. INTRODUCTION

Although it is a relatively common metal, cadmium has remained one of the most difficult to detect. The complications arising from its identification as yellow cadmium sulfide make it a very unpractical method. Cadmium, by virtue of its electronic configuration does not tend to form colored complexes easily. In this connection it must be noted that there are no crystal field stabilization effects in the cadmium ion because of the completed d orbitals.

The qualitative tests for cadmium up to 1958 have been exhaustively reviewed by Feigl[54]. Various organic reagents such as diphenyl carbazide and diphenylthiocarbazone have been employed with moderate success. The most successful of such reagents has been p-nitrodiazoaminoazobenzene which gives a violet to blue lake with cadmium. Most interfering metals can be complexed by the addition of tartrate[55].

West and Diffee[56] in 1961 proposed a test for cadmium based on the use of glyoxal bis(2-hydroxyanil). The reaction is carried out on beads of an anion exchange resin on which the cadmium has been concentrated as the tetraiodo complex. The limit of identification is 0.05 µg.

While investigating the reactions of new Schiff bases at A.U.B. it was observed that the reaction product between o-aminophenol

and pyridine 2,6 dialdehyde formed intense red colors with cadmium in alkaline solutions. Higher specificity is obtained with sodium hydroxide than with ammonia.

The most serious interferences resulted from the alkaline earth, manganese and thallium.

The following part of this thesis describes the test finally adopted for detecting cadmium.

II. EXPERIMENTAL

A.- Reagents:

Sodium fluoride saturated solution.

Sodium bisulfite 10% solution.

Sodium hydroxide 10% solution.

Chloroform.

Schiff base 2,2'-(2,6-pyridinediylbis methylidynenitrilo) diphenol.

Preparation of the Schiff base:

0.44 g. of freshly sublimed o-amino phenol is dissolved in 75 ml. of water at 100°C. To this add 0.27 g. of pyridine 2,6 dialdehyde in 25 ml. of water. The mixture is maintained in a water bath for 30 minutes, then stored overnight in the refrigerator. The yellow precipitate is filtered and washed with water, and recrystallized from methyl alcohol. M.P. 206 - 207°C. The solid reagent should be kept in a dark bottle and stored in the refrigerator when not in use. In this form this reagent is stable for many months. The reagent solution is prepared daily by dissolving 0.05 g. of solid reagent in 18 ml. of ethyl alcohol and is kept in a dark brown bottle.

Preparation of pyridine 2,6 dialdehyde:

Pyridine 2,6 dicarboxylic acid is esterified with ethyl alcohol[57]. The ester is reduced with lithium aluminum hydride to the corresponding alcohol which is oxidized with freshly prepared manganese dioxide to pyridine 2,6 dialdehyde.

Standard cadmium solutions:

A 1% cadmium solution is prepared by dissolving 1 g. of cadmium in a few drops of nitric acid and heating to get rid of oxides of nitrogen then diluting to 100 ml. with distilled water. This solution is diluted as necessary to prepare standard working solutions.

B.- Procedure:

To one drop of cadmium solution add 3 drops of reagent, 1 drop of sodium hydroxide solution or ammonium hydroxide solution, shake. Add 3 - 4 drops of chloroform. Shake. A red color appears in the chloroform layer.

Limit of detection: 0.025 µg. cadmium.

Limit of dilution : 1:2000.000.

C.- Behaviour of Cations with the Reagent:

The following table shows the behaviour of cations with the reagent using sodium hydroxide and ammonium hydroxide solutions.

Table 7

Behaviour of Cations with the Reagent

Ions	NH_4OH 1:1 solution	NaOH 10% solution
Cd(II)	intense red color extractable	intense red color extractable
Sr(II)	slight color extractable	slight color extractable

Ions	NH_4OH 1:1 solution	NaOH 10% solution
Sn(IV)	no reaction	extract slightly yellow
Cs(I)	no reaction	extract slightly yellow
Tl(I)	red color extractable	red color extractable
Pd(II)	intense red color extractable	pale red extractable
Co(II)	intense red color extractable	no reaction
Zn(II)	intense color red extractable	no reaction
Ba(II)	pale red extractable	pale red extractable
Al(III)	no reaction	pale yellow extractable
UO_2^{2+}	red not extractable	red not extractable
Fe(III)	red extractable	red not extractable
Bi(III)	red extractable	no color
Cr(III)	no reaction	no reaction
Cu(II)	extract slightly reddish	extract colorless
Ni(II)	red color extractable	extract colorless
Ca(II)	red color extractable	red color extractable
Th(IV)	red color extractable	colorless extract
Mn(II)	red extractable	red extractable
Zr(IV)	no reaction	no reaction
Be(II)	no reaction	no reaction
Mg(II)	pale red extractable	yellow extract
As(III)	colorless extract	colorless extract
Hg(I)	red extract turned black	dark color
Hg(II)	red extractable	dark color
Sb(V)	orange extract	colorless extract
As(V)	no reaction	no reaction

Ions	NH_4OH 1:1 solution	NaOH 10% solution
Ce(IV)	orange not extractable	yellow not extractable
Ag(I)	yellow not extractable	black color not extractable
Pd(II)	orange color extractable	brownish color not extractable
Au(III)	orange color extractable	black not extractable
Pt(VI)	orange extractable	orange extractable
La(III)	orange extractable	yellow not extractable
Rb(I)	yellow not extractable	yellow extractable
Rh(III)	brown not extractable	brown not extractable
Li(I)	yellow extractable	no reaction

Table 7 shows that better results are obtained with sodium hydroxide solution since only Sr(II), Tl(I), Pb(II), Ba(II), Ca(II), Mn(II) interfere while with ammonia a larger number of ions interfere.

D.- Detection of Cadmium in the Presence of Interfering Ions:

Table 7 shows that in alkaline solution nickel does not interfere while calcium does. Various tests have shown that the specificity of the reaction is pH dependent. If calcium is not to react then nickel will and vica versa. Sodium acetate was then tried, calcium did not interfere while nickel did, the latter was masked with cyanide which complexed both nickel and cadmium. The cadmium can be released by addition of chloral hydrate. This method would have been adopted had it not been for the interference of manganese(II) and permanganate ions.

In view of this and since nickel which is a serious competitor to cadmium did not interfere in basic solutions, it

was decided to resort to addition of sodium hydroxide, calcium being removed by the addition of fluoride and manganese by sodium bisulfite.

On this basis the recommended procedure then becomes:

To one drop of cadmium solution or unknown solution add 2 drops of saturated fluoride solution followed by 2 drops of sodium hydrogen sulfite 10% solution. In the presence of potassium permanganate, 3 drops of sodium hydrogen sulfite solution are added. Make the solution alkaline with 1 drop of sodium hydroxide solution 10% then add 2 drops of Schiff base and finally 3 drops of chloroform. Observe the color which is formed in the chloroform layer.

Limit of identification: 0.1 µg. cadmium.

Limit of dilution : 1:500,000.

E.- Determination of 1 µg. Cadmium(II) in the Presence of 500 µg. of Foreign Ions:

Using the above procedure tests were carried out on mixtures containing 1 µg. cadmium and 500 µg. of foreign ion. Tables 8 and 9 show the results obtained with cations and anions respectively.

Table 8

Identification of 1 µg. Cadmium in the Presence of 500 µg. of Foreign Cations

Cations	Color obtained	Cations	Color obtained
1 µg. Cd(II) + 500 µg. Ca(II)	red	1 µg. Cd(II)+500 µg. Cr(III)	red
500 µg. Ca(II)	colorless	500 µg. Cr(III)	colorless

Cations	Color obtained	Cations	Color obtained
1 µg.Cd(II)+500 µg.Mn(II)	red	1 µg.Cd(II)+500 µg.Co(II)	red
500 µg. Mn(II)	colorless	500 µg. Co(II)	colorless
1 µg.Cd(II)+500 µg.Al(III)	red	1 µg.Cd(II)+500µg.Cu(II)	red
500 µg. Al(III)	colorless	500µg.Cu(II)	colorless
1 µg.Cd(II)+500 µg.As(V)	red	1 µg.Cd(II)+500 µg.Fe(III)	red
500 µg. As(V)	colorless	500 µg. Fe(III)	colorless
1 µg.Cd(II)+500 µg.Be(II)	red	1 µg.Cd(II)+500 µg.Pb(II)	red
500 µg. Be(II)	colorless	500 µg. Pb(II)	colorless
1 µg.Cd(II)+500 µg.Ce(IV)	red	1 µg.Cd(II)+500 µg.Mg(II)	red
500 µg. Ce(IV)	colorless	500 µg. Mg(II)	colorless
1 µg. Cd(II)+500µg.Hg(II)	red	1 µg.Cd(II)+500µg.Sr(II)	red
500 µg. Hg(II)	colorless	500 µg. Sr(II)	colorless
1 µg.Cd(II)+500 µg.Ag(I)	red	1 µg.Cd(II)+500 µg.Zr(VI)	red
500 µg.Ag(I)	colorless	500 µg. Zr(VI)	colorless
1 µg.Cd(II)+500 µg.UO_2^{2+}	red	1 µg.Cd(II)+500 µg.Pd(II)	red
500 µg. UO_2^{2+}	colorless	500 µg. Pd(II)	colorless
1 µg.Cd(II)+500 µg.Zn(II)	red	1 µg.Cd(II)+500 µg.Au(III)	red
500 µg.Zn(II)	colorless	500 µg. Au(III)	colorless
1 µg.Cd(II)+500 µg.Ni(II)	red	1 µg.Cd(II)+500 µg.Th(IV)	red
500 µg. Ni(II)	colorless	500 µg. Th(IV)	colorless
1 µg.Cd(II)+500 µg.La(III)	red	1 µg.Cd(II)+500 µg Pt(VI)	red
500 µg. La(III)	colorless	500 µg. Pt(VI)	colorless
1 µg.Cd(II)+500 µg.Rb(I)	red	1 µg.Cd(II)+500 µg.Li(I)	red
500 µg. Rb(I)	colorless	500 µg. Li(I)	colorless

Cations	Color obtained	Cations	Color obtained
1 µg.Cd(II)+500 µg.Cs(I)	red	2 µg.Cd(II)+500 µg.Rh(III)	red
500 µg. Cs(I)	colorless	500 µg. Rh(III)	colorless
2.5µg.Cd(II)+500µg.Bi(III)	red	2 µg.Cd(II)+500µg.Ba(II)	red
500 µg. Bi(III)	colorless	500 µg. Ba(II)	colorless
1 µg.Cd(II)+500 µg.Tl(I)	red		
500 µg. Tl(I)	red		

No interference is observed except for thallium. To avoid the interference of Tl(I) 6 drops of 10% chloride solution are added.

The limit of identification of cadmium(II) in the presence of 500 µg. Rh(III), Ba(II), and Bi(III) is 2 µg., 2 µg. and 2.5 µg. respectively.

Table 9

Identification of 1 µg. Cadmium(II) in the Presence of 500 µg. of Anions

Ions	Color obtained	Ions	Color obtained
1µg.Cd(II)+500µg.$CO_3^=$	red	1µg.Cd(II)+500µg.Br^-	red
500 µg. $CO_3^=$	colorless	500 µg. Br^-	colorless
1 µg.Cd(II)+500µg.$CrO_4^=$	red	1 µg.Cd(II)+500µg.$B_4O_7^=$	red
500 µg. $CrO_4^=$	colorless	500 µg. $B_4O_7^=$	colorless
1 µg.Cd(II)+500µg.Cit.$^{3-}$	red	1 µg.Cd(II)+500µg.$Cr_2O_7^=$	red
500 µg. cit.$^{3-}$	colorless	500 µg. $Cr_2O_7^=$	colorless
1 µg.Cd(II)+500µg.BrO_3^-	red	1 µg.Cd(II)+500µg.Cl^-	red
500 µg.BrO_3^-	colorless	500 µg. Cl^-	colorless

Ions	Color obtained	Ions	Color obtained
1 µg.Cd(II)+500µg.ClO_4^-	red	1 µg.Cd(II)+500µg.IO_4^-	red
500 µg. ClO_4^-	colorless	500 µg. IO_4^-	colorless
1 µg.Cd(II)+500µg.$Mo_7O_{24}^=$	red	1 µg.Cd(II)+500µg.$HPO_4^=$	red
500 µg. $Mo_7O_{24}^=$	colorless	500 µg. $HPO_4^=$	colorless
1 µg.Cd(II)+500µg.$[Fe(CN)_6]^=$	red	1 µg.Cd(II)+500µg.IO_3^-	red
500 µg.$[Fe(CN)_6]^{4-}$	colorless	500 µg. IO_3^-	colorless
1 µg.Cd(II)+500µg.oxalate$^=$	red	1 µg.Cd(II)+500µg. $Fe(CN)_6^{4-}$	red
500 µg. oxalate$^=$	colorless	500 µg. $[Fe(CN)_6]^{3-}$	colorless
2 µg.Cd(II)+500µg.CN^-	red	2.5µg.Cd(II)+500µg.MnO_4^-	red
500 µg. CN^-	colorless	500 µg. MnO_4^-	c olorless

1 µg. cadmium can be identified in the presence of 500 µg. of anions with the exception of CN^- and MnO_4^- when the limits are 2 µg. and 2.5 µg. respectively.

F.- Detection of Cadmium in Various Mixtures:

In the following set of experiments, the same procedure was applied for the detection of cadmium in seven different solutions each containing at least 4 cations. Standard solutions containing 1% of the cations were prepared (i.e. 500 µg. per drop) one drop from each solution was taken and mixed in a test tube.

Results are shown in table 10 below.

Table 10

Detection of Cadmium in Various Mixtures

Mixtures of ions	Color obtained
Ag+Co+Fe+Ni+Cd	red

Mixtures of ions	Color obtained
Ag + Co + Fe + Ni	colorless
Sr + Hg(I) + K + Ba + Na + Cd	red
Sr + Hg(I) + K + Ba + Na	colorless
Cu + Ca + Li + Mn + Pb + Cd	red
Cu + Ca + Li + Mn + Pb	colorless
Hg(II) + As + Zn + UO_2^{2+} + Sb + Cd	red
Hg(II) + As + Zn + UO_2^{2+} + Sb	colorless
Bi + Ce + Cr + Al + Be + Cd	red
Bi + Ce + Cr + Al + Be	colorless
Zr + Mg + Pt + Pd + Au + Cd	red
Zr + Mg + Pt + Pd + Au	colorless
Rh + Rb + Th + La + Cs + Cd	red
Rh + Rb + Th + La + Cs	colorless

The procedure described above was finally tested by detecting cadmium in a solution containing 38 other ions. This solution was prepared by taking a drop from each of the 38 cations mixed with 1 drop of 1% cadmium. A solution containing the same cations but without cadmium was also prepared.

Solution (1): Ag(I) + Co(II) + Fe(III) + Ni(II) + Sr(II) + Hg(I) + Na(I) + K(I) + Ba(II) + Th(I) + Pt(VI) + Pd(II) + Cu(II) + Ca(II) + Mn(II) + Pb(II) + Li(I) + Hg(II) + As(V) + U(VI) + Sb(III) + Bi(III) + Ce(IV) + Be(II) + Cr(III) + Zr(IV) + Al(III) + Rh(III) + Rb(I) + Zn(II) +

$Mo(VI) + V(V) + MnO_4^- + CN^- + Mg(II) +$

$Au(III) + Cs(I) + La(III)$.

Solution (2): Solution (1) + Cd(II).

Results: Solution (2) produced a red color while solution (1) gave a colorless chloroform layer.

These results are extremely satisfactory and show that the procedure is functional and can be applied for the detection of cadmium in the presence of a very large number of foreign ions.

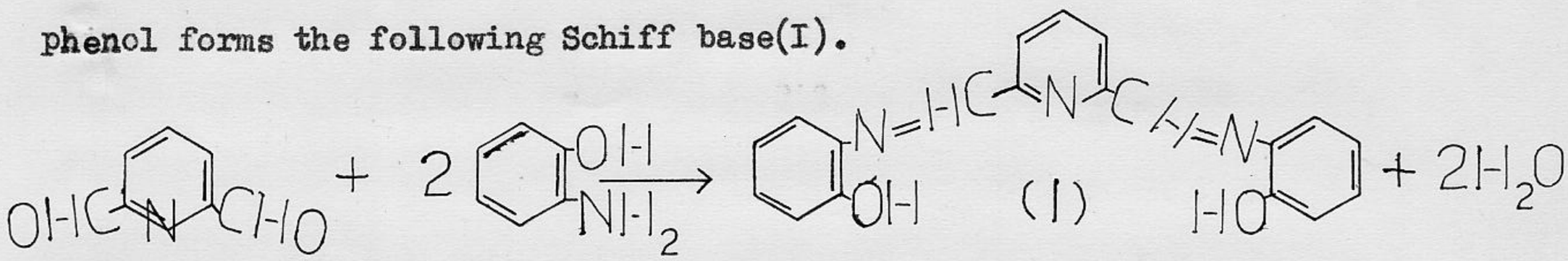
III. DISCUSSION

The ability of metal ions to form chelates is relatively general and for a particular chelating agent, the stability of chelates formed changes only gradually from one metal to another. Consequently it would seem unlikely that a chelating agent could be specific for a single metal ion. However, some remarkable agents for concentrating metals occur in nature. Hemoglobin molecules concentrate iron in blood; the vanadium in the blood of the sea squirt is a million fold that of the ocean water in which it lives, and the blood of the octopus contains 100,000 times as much copper as its surroundings. A reasonable hypothesis is that organic complexing agents are specifically sequestering one ion. Selectivity for a single metal ion has not yet been achieved and while the probability of synthesizing a chelating agent which displays absolute specificity seems at present remote,considerable research is being undertaken towards this end. Among promising reagents that have been synthesized are the group variously called anils, imines or azomethines, but best known as Schiff bases after the worker who first synthesized them in 1864.

Schiff bases have the general structures -RC=NR', where R and R' are alkyl, cycloalkyl, aryl or heterocyclic radicals and may be variously substituted. Schiff bases are prepared by the condensation of a primary amine with an active carbonyl group. To be effective as chelating agents Schiff bases must include a functional group appropriately located so that a five or a

six-membered ring can be formed upon reaction with a metal ion.

The condensation of pyridine 2,6 dialdehyde with o-amino-phenol forms the following Schiff base(I).



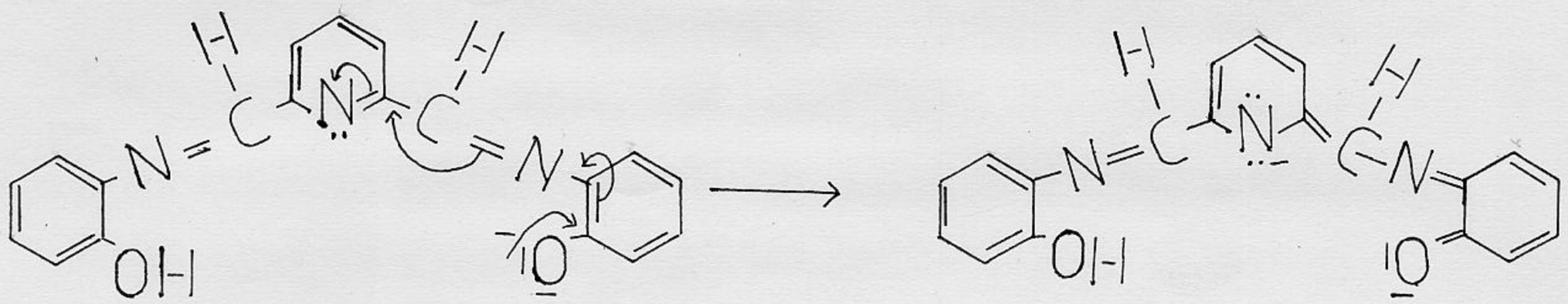
Analyses of the structure and of atomic models of the Schiff base shows that it is planar.

In the absence of a study of the nature of the complex formed with cadmium and its empirical formula it is difficult to postulate a definite structure for the complex.

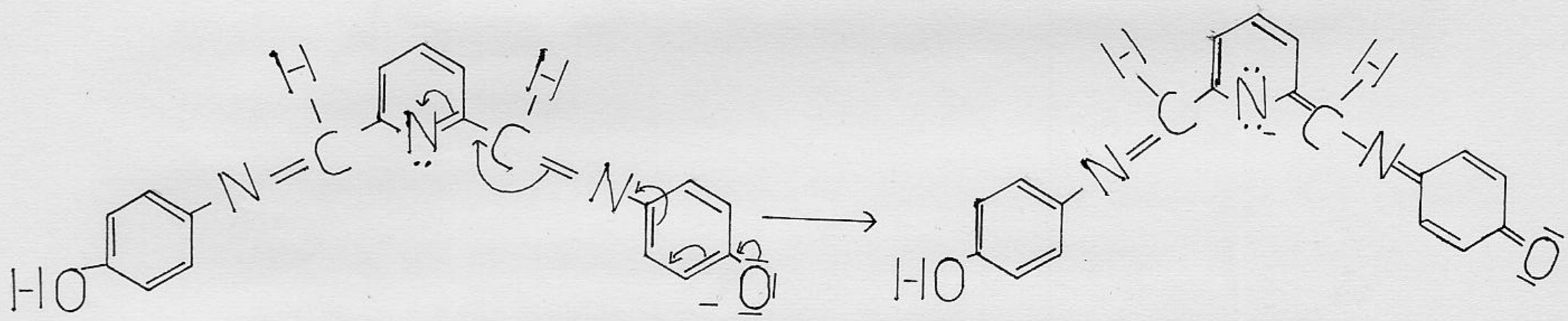
By analogy to similar cases, the possibility of formation of a salt like complex should be considered since the reaction is carried out in alkaline solution. On the other hand there is evidence that the $\bar{1}0\bar{1}^{-}$ is not acting as a center of coordination. Thus with p-aminophenol a Schiff base is obtained where the OH groups are in a most unfavorable position to coordinate with the metal ions and yet stable red colored complexes are formed with cadmium. It also appears that with m-aminophenol, a Schiff base is formed which does not form colored complexes with cadmium and other metals. These observations, plus the fact that the color of the complexes formed with various metals is always red might be a clueto the phenomenon responsible for the color.

If one remembers that both Schiff bases obtained with ortho and para aminophenols are capable of resonating as in (II) and (III) while the meta cannot resonate, a possible explanation

can be put to explain the behaviour of the reagent.



(II)



(III)

The quinoid structure and the conjugate system obtained could thus be responsible for the red color formed with the Schiff base obtained from ortho and para aminophenols only. According to this argument the Schiff base obtained with meta aminophenol should not give colored complexes which is in agreement with the experimental result[58].

It would therefore seem that color formation arises from a phenomenon of resonance and conjugation following chelation.

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