A NEW SPECIFIC METHOD FOR THE MICRODETECTION OF URANIUM AND ANTIMONY

BY

SONIA B. ADROUNI

A NEW SPECIFIC METHOD FOR THE MICRODETECTION OF URANIUM AND ANTIMONY

BY

SONIA B. ADROUNI

submitted in partial fulfillment of the requirements
for the degree Master of Science
in the Chemistry Department of the
American University of Beirut
Beirut, Lebanon
June 1967

ACKNOWLEDGMENT

The author wishes to express her deep gratitude to Professor Samir K. Thabet who initiated the problem and guided this work with steady interest and enthusiasm.

The author is also indebted to the Research Committee of the School of Arts and Sciences for financial aid in support of this work.

ABSTRACT

In this work the Schiff base: 2,2'[2,6-pyridinediylbis (methylidynenitrilo)] diphenol, obtained from the condensation of 2,6-pyridine dicarboxaldehyde and o-aminophenol is proposed for the sensitive and specific detection of U(VI), Sb(III) and Bi(III) in the presence of other ions. Procedures are presented for masking the effect of interfering ions.

The identification limits for U(VI), Sb(III) and Bi(III) are 0.05μg, 0.05μg and 0.5μg respectively. Procedures are proposed for detecting these ions in various mixtures and in the presence of a large number of foreign cations.

Antimony (III) reacts with the Schiff base, whereas antimony (V) fails to do so. Both antimony and bismuth can be detected in pharmaceutical products.

A mechanism for the formation of the colored chelates is also proposed.

TABLE OF CONTENTS

Page

CHAPTER I

CHAPTER II

LIST OF TABLES

CHAPTER I

INTRODUCTION

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 concentration in the blood of the sea squirt, Phallusia mamillata, 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. On this basis, Bayer (1) has stated: "In nature the specifically concentrated metal ions are all bound in organic complexes. Thus, the simplest explanation for the selective concentration appeared to be the hypothesis that the organic complexing agents are specific for only one ion. Selectivity for a single metal ion has not yet been achieved with synthetic chelating agents."

The probability of synthesizing a chelating agent displaying absolute specificity seems at present remote, but considerable research is being undertaken towards this end. With more knowledge of the properties of functional groups and the nature of donor and central atoms, more selective and more sensitive reagents are being continuously prepared. Among such promising reagents 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 structure $-RC=NR'$, 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 six-membered ring can be formed upon reaction with a metal ion.

Because Schiff bases are relatively easy to prepare and because of their synthetic flexibility, they can be obtained with widely varied substitution by selection of the appropriate reactants. By changing the nature and the position of donor atoms and groups it is possible to control the size of chelate rings formed and to exploit the effect of substitution. All these and other factors make Schiff bases interesting analytical reagents in general and, with appropriate structure, chelating agents of great potential value for analytical applications.

The analytical applications of Schiff bases have been extensively discussed and reviewed by Jungreis and Thabet(2). It appears though, that Schiff bases have found limited applications in the field of ultra-micro analytical work.

The main objective of this work was to develop new reagents that show specific and sensitive reactions with uranium antimony and bismuth. These ions were chosen because no satisfactory method has so far been reported for their trace analyses. This is to be expected in view of their electronic configuration. It was thought that in order to promote the formation of a colored chelate with uranium, antimony and bismuth, the most favourable conditions have to be satisfied by the chelating agent, namely the possibility of forming fused five membered rings, and extended resonance. These conditions seemed to be satisfied with the Schiff base 2,2' [2,6-pyridinediylbis (methylidynenitrilo)] diphenol, obtained from condensing 2,6-pyridine dicarboxaldehyde with o-aminophenol. This Schiff base reacts with uranium, antimony and bismuth in acidic medium to yield intensely colored products extractable in chloroform. Only vanadium gives a red color not extractable in chloroform. All the other cations that were tested and gave colors, lost their color in acid solution. It was therefore comparatively easy to develop a specific test for each of these three cations.

The tests that are described in this work present a number of advantages over the reported methods:

1.- Their sensitivity and selectivity are superior.

2.- They have relatively few interfering cations.

3.- They are not affected by anions.

4.- The colored products are extractable in chloroform.

5.- The methods permit the detection of each of these ions in a mixture of a very large number of cations.

6.- The same reagent can be used for each ion, provided the reactions are "conditioned".

The most serious disadvantage of the method is the difficulty in securing 2,6-pyridine dicarboxaldehyde. This used to be easily available, but its production has been discontinued by a number of manufacturers. It can however be prepared from 2,6-pyridine diester (3).

The work in this thesis will be presented in three separate parts, each dealing with the historical and experimental work related with a particular ion.

CHAPTER II

PART ONE: URANIUM TEST

A. Historical:

A review of the literature reveals that a large number of tests have been reported for uranium (VI). Essentially these tests are based on precipitation, complex formation and fluorescence.

In hydrochloric acid solution U(VI) and U(IV), in concentrations above 200μg form a green precipitate upon addition of EDTA, NH_4F and $FeSO_4$. Other heavy metal cations interfere with this test (4). A more sensitive precipitating agent for U(VI) with a limit of 2.5μg is $Co(NH_3)_6Cl_3$. Be(II), Ti(IV), In(III), Ga(III) and Zr(IV) interfere however (5).

In neutral or acidic solutions of U(VI) salts, $K_4[Fe(CN)_6]$ gives a red brown precipitate. Only Cu(II) and Fe(III) interfere by giving a brown color and Prussian blue respectively. The interference can be removed by reducing ferric and copper ions with iodide, or precipitating interfering ions with carbonate leaving uranyl in solution as soluble uranyl carbonate complex. The limit of identification is 0.92μg. (6) The procedure can be modified to detect uranium in minerals containing up to 0.2% uranium in 0.2 g samples. (7)

Oxine gives a red brown precipitate in alkaline carbonate solution with more than 10μg U(VI). All possible interfering ions are precipitated with carbonate. A separation of the precipitate and the solution is therefore necessary (8).

A filter paper procedure for detecting uranium (VI) has also been reported. The filter paper is treated with $K_4[Fe(CN)_6]$ and $Mn(NO_3)_2$, upon spotting with uranyl ions, an orange color will appear. The limit of identification is 0.15μg. Ag(I), Cu(II), Fe(III), Hg(II), Co(II) Ni(II), Zn, Cd, Bi, and Sn(IV) interfere with the test (9).

A specific test for U(VI) is described by M.P. Pavlovskaya and co-workers. They use 2-quinolinol in pyridine which gives a red color with U(VI) in concentrations greater than 177.5μg/2ml. All interference is removed at pH 5.3 by Complexon III (10).

Bayer (11) has reported that Schiff bases obtained from aminophenols and thiophenols with aromatic or aliphatic dicarbonyl compounds have selective affinities for Ni, Cu(II), Ba and especially U(VI). Glyoxal and o-aminophenol condense to give a Schiff base which complexes uranyl ion selectively; however no further work seems to have been done, although a spectrophotometric method for determining uranium using the Schiff base was reported by Bayer (12).

Rhodamin B reacts with Fe(III), Bi, and U(VI) in neutral solutions to produce a red color. The benzene extract gives an intense orange fluorescence in ultra-violet light. The limit is 0.05μg (13). A yellow fluorescence is obtained at U(VI) concentrations greater than 0.05μg with Na_3PO_4 (14). Fluorescence produced by the fusion of NaF with uranyl ions on a platinum loop provides a very sensitive test for uranium with a limit of 0.001μg in 0.001 ml; Fe(III), Mn(II), Th(IV), and Be interfere (15).

Uranyl ions in concentrations greater than 2.5μg can also be detected by the quenching of the red fluorescence of cochineal (16).

The decomposition of oxalic acid to formic acid in the presence of U(VI) has been attributed to the photolytic activity of the latter. The formic acid produced, reduced $HgCl_2$ to finely divided mercury in the presence of acetic acid and ammonia. The limit of identification is 2.5μg (17).

Jungreis and Ben Dor (18) have described what seems to be the best reported test for uranium (VI). At pH 2-3 the Schiff base obtained from p-dimethylaminoaniline and salicylaldehyde reacts with uranyl ions to give a red color for concentrations of uranium greater than 1 ppm. Only Fe(III) interferes by giving a blue-violet color through reaction with salicylaldehyde.

Feigl (19) gives a list of tests which are of little importance in view of their lack of selectivity and sensitivity. For example, quercetin, fluorescein, and phthalimide dioxime (20) all give with U(VI) red colors under different experimental conditions. A large number of ions interfere, however. Several other organic reagents are used in the detection of uranium (21-30). None of these are specific or sensitive enough for its microdetection.

B. Experimental:

1.- Preparation of the Reagent

The reagent is prepared by the following method: 0.44 g of freshly sublimed o-aminophenol is dissolved in 75 ml of water at 100°C. To this add 0.27 g of 2,6-pyridine dicarboxaldehyde in 25 ml of water. The pyridine 2,6-dicarboxaldehyde was obtained through the University of Illinois from Raschig Co., Germany. 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 methanol. The yield is 78%. The solid reagent is stored in a dark bottle kept in the refrigerator.

The reagent solution is prepared by dissolving 30 mg of solid reagent in 10 ml chloroform and is kept in dark brown bottle provided with a dropper.

2.- Detection of U(VI)

To one drop of the test solution add four drops of 0.3% solution of the reagent in chloroform, shake the test tube and add a drop of glacial acetic acid, shake again. Add about one ml of water. A thick red precipitate is formed at high concentrations of Uranium (VI), whereas at low concentrations a red color is obtained which is extractable in chloroform. 0.05μg uranium (VI) can be detected by comparing the test solution with a blank which gives a pale yellow color in the chloroform layer.

Limit of identification: 0.05μg U(VI).

Limit of dilution: 1:1,000,000.

Reagents: 0.3% solution of the reagent in chloroform.
Glacial acetic acid.
Chloroform.

3.- Effect of Reagent on Other Cations

Table 1, shows the colors obtained when the procedure described above is applied to various cations. In each case a drop of the test solution containing 500μg of the cation is used

Table I

Colours Obtained with Various Cations

Cations	Color in the absence of HAc	Color in the presence of HAc
Li(I)	yellow	yellow
Na(I)	yellow	yellow
K(I)	yellow	yellow
Rb(I)	yellow	yellow
Cs(I)	yellow	yellow
Be(II)	yellow	yellow
Mg(II)	yellow	yellow
Ca(II)	yellow	yellow
Sr(II)	yellow	yellow
Ba(II)	yellow	yellow
Zr(IV)	yellow	yellow
V(V)	yellow red in water	yellow red in water
Cr(III)	yellow	yellow
Mo(VI)	yellow	yellow
W(VI)	yellow	yellow
Mn(II)	pink	pale pink
Fe(III)	yellow red in water	yellow red in water
Co(II)	red	yellow
Ni(II)	pink	yellow
Pd(IV)	yellow	yellow
Rh(II)	yellow	yellow

Table 1, continued

Cations	Color in the absence of HAc	Color in the presence of HAc
Pt(IV)	yellow	yellow
Cu(II)	yellow	yellow
Ag(I)	yellow	yellow
Au(III)	brown-red	brown
Zn(II)	red	yellow
Cd(II)	yellow	yellow
Hg(I)	yellow	yellow
Hg(II)	yellow	yellow
Al(III)	yellow	yellow
Tl(I)	yellow	yellow
Sn(II)	red	pale red
Sn(IV)	pale red	yellow
Pb(II)	yellow	yellow
As(III)	yellow	yellow
As(V)	yellow	yellow
Sb(III)	yellow	red(discharged)
Bi(III)	red	red
La(III)	yellow	yellow
Ce(III)	yellow	yellow
Ce(IV)	yellow	yellow
Th(IV)	yellow	yellow
U(VI)	red	red

It is apparent from the above results that the presence of glacial acetic acid increases the specificity of the test for uranium. Color interference by the cations are not significant except for Bi(III). Further investigations were therefore undertaken to eliminate the interference from bismuth without affecting the sensitivity of the uranium test.

4.- Effect of Reagent on Anions

To test for the effect of the various anions (1% solutions) on the uranium test, two sets of experiments were carried out. In the first set, a drop of each of the anion solutions was treated as in the procedure described above. In the second set the procedure was repeated in the presence of 0.5µg U(VI).

The results are summarized in Table 2.

Table 2

Colors Obtained with Anions

Anions	Anions alone	Anions + U(VI)
F^-	yellow	red
Cl^-	yellow	red
Br^-	yellow	red
I^-	yellow	red
NO_3^-	yellow	red

Table 2, continued

Anions	Anions alone	Anions + U(VI)
$SO_4^=$	yellow	red
$S^=$	yellow	red
$S_2O_3^=$	yellow	red
CN^-	yellow	red
$CO_3^=$	yellow	red
$PO_4^≡$	yellow	red
Citrate	yellow	red
Tartrate	yellow	red
Malonate	yellow	red
EDTA	yellow	red
CNS^-	yellow	red
$CrO_4^=$	yellow	red
MnO_4^-	yellow	red
Oxalate	yellow	yellow

Table 2 shows that 0.5μg U(VI) can be detected in the presence of 1000 times its concentration of foreign anions with the exception of oxalate which prevents the detection of uranium at concentrations below 500μg.

5.- Detection of U(VI) in the Presence of Foreign Cations.

To prevent the interference of bismuth, see Table 1, the conditions of the test were varied. Several acids were tried instead of glacial acetic acid; thus nitric, hydrochloric, citric, malonic and phosphoric acid either failed to remove bismuth or masked both bismuth and uranium, or produced interference from other ions such as gold(III), Sn(II). Even 3N and 6N acetic acid proved to be less satisfactory than glacial acetic acid.

Various masking agents were also tried in an attempt to prevent the reaction with bismuth. Thiourea was found to be the most suitable. It did not reduce the sensitivity limit while it removed the interference of bismuth. Although thiourea forms yellow complexes with several cations, none of them were found to be extractable in chloroform.

Procedure: To one drop of the test solution, add one drop of saturated thiourea solution in water and one drop of glacial acetic acid. Shake well. Add three drops of 0.3% of the Schiff base in chloroform followed by one to two ml of water. Observe color in chloroform layer. Vigorous shaking is recommended for better results.

Limit of identification: 0.05 μg U(VI).

Limit of dilution: 1:1000,000.

Reagents: 0.3% reagent in chloroform.

Saturated solution of thiourea in water.

Chloroform.

Glacial acetic acid.

The procedure described above was applied to the cations listed in Table 1. None of the cations interfered by giving a color in the chloroform layer. Thiourea was therefore adopted as a masking agent for bismuth.

6.- Limits of Identification of U(VI) in the Presence of Foreign Ions

The work described above has shown that thiourea did not affect the identification limit of the uranium test which remained at 0.05µg. It was therefore desirable to determine quantitatively the sensitivity of the uranium test in the presence of foreign ions. For this purpose, two sets of experiments were carried out. In the first, the procedure described above was applied without thiourea while in the second set thiourea was used. In all cases, the concentration of the foreign ion was maintained at 500µg while the concentration of uranium was decreased until the limit of isentification could be clearly determined.

Table 3

Limits of Identification of U(VI) in the Presence of Foreign Cations

Cations	Limits without Thiourea in µg	Limits with Thiourea in µg
Li(I)	0.05	0.05
Na(I)	0.05	0.05

Table 3 - continued

Cations	Limits without Thiourea in µg	Limits with Thiourea in µg
K(I)	0.05	0.05
Rb(I)	0.05	0.05
Cs(I)	0.05	0.05
Be(II)	0.1	0.1
Mg(II)	0.1	0.05
Ca(II)	0.1	0.05
Sr(II)	0.1	0.05
Ba(II)	0.1	0.05
Zr(IV)	0.1	0.1
V(V)	0.5	0.5
Cr(III)	0.1	0.05
Mo(VI)	0.05	0.05
W(VI)	0.1	0.05
Mn(II)	0.5	0.1
Fe(III)	0.05	0.05
Co(II)	0.1	0.05
Ni(II)	0.05	0.05
Pd(IV)	0.05	0.05
Pt(IV)	0.05	0.05
Cu(II)	0.1	0.05
Ag(I)	0.5	0.1
Au(III)	0.5	0.2
Zn(II)	0.05	0.05
Rh(II)	0.05	0.05

Cations	Limits without Thiourea in µg	Limits with Thiourea in µg
Cd(II)	0.5	0.1
Hg(I)	0.5	0.1
Hg(II)	0.2	0.1
Al(III)	0.05	0.05
Tl(I)	0.05	0.05
Sn(II)	0.5	0.1
Sn(IV)	5	0.1
Pb(II)	0.1	0.05
As(III)	0.1	0.05
As(V)	0.05	0.05
Sb(III)	---	---
Bi(III)	---	0.1
La(III)	0.05	0.05
Ce(III)	0.05	0.05
Ce(IV)	5	0.5
Th(IV)	0.1	0.05

A number of interesting facts appear from Table 3.

1.- In no case does the addition of thiourea decrease the sensitivity of the uranium test.

2.- On the contrary the limit of identification is improved in a very large number of cases.

3.- In the absence of thiourea it is not possible to determine U(VI) when bismuth is present, while in the presence of thiourea 0.1µg U(VI) can be clearly determined in the presence of 5000 times as much bismuth.

5.- Surprisingly, Sb(III) which does not form a color with the reagent (Table 1) prevented the detection of uranium, and even thiourea did not mask it. This is probably due to the fact that the very high acidity of the antimony solution caused the uranium chelate to decompose. This is to be expected since it was shown that mineral acids prevent the formation of the uranium chelate. A buffer was therefore needed to prevent the damaging effect of the acid antimony. A number of buffers were tried and it was found that a 20% solution of tartrate masked the antimony.

When antimony is present the following procedure is therefore recommended: add two drops of a 20% solution of potassium sodium tartrate to a drop of test solution containing Sb(III) and U(VI). Follow this with two drops of glacial acetic acid. Shake well and observe the color. It is possible to detect 0.5µg U(VI) in the presence of 500µg Sb(III).

This is not a serious obstacle since the same reagent can be used to prove the presence of antimony (see Part Two).

6.- In a large number of cases it is possible to detect uranium at concentrations as low as 0.05µg in the presence of 10,000 times its concentration of foreign ion.

7.- Detection of U(VI) in Mixtures of Foreign Ions

In the following set of experiments U(VI) was detected in seven different solutions each containing at least six cations. Standard solutions containing 1% of the cation are prepared (i.e. 500µg per drop). Take one drop from each solution and mix in a test tube. Add ten drops of glacial acetic acid and 5 drops of thiourea to each mixture and shake well, and follow this with 10 drops of the reagent. Observe the color in the chlorform layer. The same procedure is applied to mixtures containing the same cations and one drop of 1% U(VI). The results of these experiments are summarized in Table 4.

Table 4

Detection of Uranium in Various Mixtures

Mixtures of Ions	Color
Cu(II)+Co(II)+Mn(II)+Ni+Fe(III)+Cd+Sn(II)	yellow
Cu(II)+Co(II)+Mn(II)+Ni+Fe(III)+Cd+Sn(II)+U(VI)	red
Zn+Ba+Tl(I)+Sr+Ca+Al+Pt(IV)	yellow
Zn+Ba+Tl(I)+Sr+Ca+Al+Pt(IV)+U(VI)	red

Table 4 - continued

Mixtures of Ions	Color
Li+W(VI)+Pb+K+Hg(II)+Cs+Cr(III)	yellow
Li+W(VI)+Pb(II)+K+Hg(II)+Cs+Cr(III)+U(VI)	red
Hg(I)+Cr(III)+Zr(IV)+Mg+As(V)+Pd(II)	yellow
Hg(I)+Cr(III)+Zr(IV)+Mg+As(V)+Pd(II)+U(VI)	red
V(V)+Au(III)+Na+Ce(IV)+Ag(I)+Be+Zn	yellow
V(V)+Au(III)+Na+Ce(IV)+Ag(I)+Be+Zn+U(VI)	red
Sn(IV)+Rh(III)+Ce(III)+Th(IV)+La(III)+Rb(I)	yellow
Sn(IV)+Rh(III)+Ce(III)+Th(IV)+La(III)+Rb(I)+U(VI)	red

A similar experiment to see the effect of Sb(III) was also carried out, by adding 2 drops of 20% tartrate.

Sb(III)+Ce(IV)+Sn(II)+Bi+Pt(IV)+Pd(II)	yellow
Sb(III)+Ce(IV)+Sn(II)+Bi+Pt(IV)+Pd(II)+U(VI)	red

The procedure described above was finally tested by detecting U(VI) in a solution containing all the cations listed in Table 1. This solution was prepared by taking a drop from each cation mixed with 5 drops of 1% uranium. The procedure adopted is the following: To the mixture add 18 drops glacial acetic acid, 10 drops of thiourea, two drops of 20% tartrate and 10 drops of the reagent.

Solution (1): Li + Na + K + Rb + Cs + Be + Mg + Ca +
Sr + Ba + Zr(IV) + V(V) + Cr(III) + Mo(VI)

W(VI) + Mn(II) + Fe(III) + Co(II) + Ni +
Pd(II) + Pt(IV) + Cu(II) + Ag + Au(III) +
Zn + Cd + Hg(I) + Hg(II) + Al + Tl(I) + Rh(II)
Sn(II) + Sn(IV) + Pb(II) + As(III) + As(V)
+ Sb(III) + Bi + La(III) + Ce(III) + Ce(IV)
Th(IV).

Solution (2): Solution (1) + U(VI).

Results: Solution (2) produced a red color while solution (1) gave a yellow color.

These results are extremely satisfactory and show that the test can be applied for the detection fo uranium in the presence of a very large number of foreign ions.

The sensitivity and specificity achieved by this test make it superior to hitherto reported procedures.

PART TWO: ANTIMONY TEST

A. Historical:

Feigl (31) gives an excellent review of the various methods for the detection of antimony up to 1960. Several other tests have also been reported in the literature for Sb(III), Sb(V) and Sb(-III). They can be classified into the following groups:

a) Reduction of Sb(III) to antimony metal or SbH_3.

b) Oxidation of Sb(III) to Sb(V).

c) Precipitation reactions.

d) Complex forming reaction.

e) Luminescence reactions.

Antimony compounds are reduced to antimony metal by nascent hydrogen on a platinum rod giving a brown stain. Arsenic and tin compounds do not interfere. The limit of identification with this test is 20μg (32). Antimony compounds can also be reduced to the metal by shaking with silver powder at room temperature. However arsenic, bismuth, tellurium and copper also precipitate and a preliminary separation of these cations is necessary (33).

Hydrogen from a hydrogen generator will reduce antimony compounds at concentrations 10-200μg to SbH_3 which is fixed on $AgNO_3$ paper as a black spot (34). A modification of this procedure, improving the limit to 1μg antimony in 5 ml solution is described by Cinhandu (35). SbH_3 is bubbled through $AgHNO_2SC_6H_4CO_2Na$ giving a grayish yellow to dark brown sol.

The reducing power of antimony itself has also been used for its detection. It reduces complex phosphomolydic acid to molybdenum blue, and the limit is 0.2μg. Sn(II) is the only interfering cation.(36)

Sb(III), upon oxidation with concentrated HNO_3 is converted to Sb(V). The latter is specifically identified with Rhodamin B which produces a violet color extractable in benzene. The limit of identification is 2.5μg antimony in 5 ml of final solution (37).

When oxime is added to a drop of Sb(V) solution in a Perspex spot plate placed over black paper, yellow crystals are formed. Sb(III) is oxidized to Sb(V) with H_2O_2 and using such techniques, the limit of identification is 60μg. The test can be applied in the presence of fifteen fold excess of Cu(II), Pb(II), Zn(II) and Sn(IV) (38).

Sb(V) in concentrations greater than 5μg per ml could also be detected by extraction of $SbCl_6^-$ with toluene to give a green color, Sn(II) and As(V) do not interfere (39).

Antimony can also be identified through precipitation with both organic and inorganic reagents.

The fact that antimony salts are hydrolyzed at a lower pH than interfering Bi(III) and other H_2S group cations can be used to detect antimony in the presence of bismuth. Thus the SbOCl and the $SbOCl_2$ formed during hydrolysis give an orange precipitate with sulfide ions. Bismuth does not interfere up to a ratio of Bi:Sb of 100:1 (40).

Addition of thiosulfate to Sb(III) produces a dark red precipitate in the presence of EDTA at pH 4-5 and in boiling solution. The limit is 10 ppm. The sensitivity is however, reduced in the presence of several ions, their limiting proportions for clear detection being 4 times as much of Hg(I), 20 of Hg(II), 8 of Ag, 15 of Cu(II), 40 of Bi, 40 of As(III), 80 of As(V) and 94 of Mo(VI) (41). The specificity of the test was subsequently improved by neutralizing the solution with ammonium hydroxide and adding EDTA in the form of a 5% solution until all the precipitate dissolved. An orange red precipitate was formed by boiling the solution with solid $Na_2S_2O_3$ (4).

$NH_4[Cr(CNS)_4(NH_3)_2]H_2O$ is a useful reagent for precipitating Ag, Pb(II), Hg(I) & (II), Sb(III), Sn(II), Bi, Cu(I) Cd, Au(III), Pd(II), and Tl(I). These cations can be differentiated by the variation in the manner of precipitation in each case.(42). Evidently greater selectivity would be required.

Sb(III) salts in acid solution react with aromatic o-dihydroxy compounds, to produce slightly soluble white or pale yellow crystalline precipitates. However the yellow dyestuff, 9-methyl,2,3,7, trihydroxy 6-fluorone gives a red precipitate with Sb(III) at concentrations greater than 0.2μg. A number of other heavy metal ions interfere with this test in neutral or weakly acid solutions. In 1N HCl Mo(VI), Ge(IV), and Sn(IV) react giving orange to orange red colors (43).

1-(2-pyridylazo-2-naphtol), that is PAN, is another reagent used for spot testing Sb(III). Colors are produced on iqn exchange resins at a pH range of 4.7-6.0. Sb(III) is detected and identified under a microscope by observing the manner of crystal formation (44).

Similarly, dibenzofuran-2-sulfonic acid which precipitates 33 cations, each having characteristic crystals, can be used for the qualitative detection of antimony (45). Obviously such tests are of little practical use.

Paper chromatographic separation of Sb(III),As(III) and Sn(II) using HCl-BuOH solvent is proposed in two separate methods, the cations are detected by ammonium sulfate (46), or by dithizone (47).

Among the complex forming reactions, the following seem to be satisfactory for detecting antimony. Sb(V) gives a blue color with diphenylbenzidine or diphenylamine solution in sulfuric acid; a black or gray color is produced with Sb(III) and $Hg(CN)_2$, in alkaline medium. A modified procedure is proposed to detect Sb(III) in the presence of Sn(II) and other thioanions (48).

Alkaline solution of $3,4(OH)_2C_6H_3N{:}NPh$ (phenylazopyrochatecol) added to a solution containing more than 0.53 g/ml of Sb(III) produce a red violet color. Sn(IV) interferes, but can be masked with phosphoric acid. The anions bromate, iodate, dichromate, sulfide, and tartrate interfere with this test and tartrate prevents the reaction (49).

Feigl (50) has described a flame test, to detect extremely small amounts of antimony, which imparts a green blue luminescence to a hydrogen flame. K.P. Stolyarov and coworkers also report a method for detecting antimony, tin, and arsenic by luminescent reactions (51).

It thus appears that few of the tests for antimony enjoy specificity while the sensitivity, in general, is not too good. Tests based on luminescence properties, while showing extremely low identification limits, are not by any means specific. On the other hand the Rhodamine B test which is specific for Sb(V) is not sensitive.

B. Experimental:

1.- Preparation of the Reagent

The reagent is the same Schiff base used for the uranium test.

The reagent solution is prepared by dissolving 40mg of the Schiff base in 10ml chlorform and is kept in a dark brown bottle provided with a dropper.

2.- Detection of Sb(III)

To one drop of the test solution in a test tube, add a drop of 0.3 N HCl, four drops of the chloroform solution of the reagent and 1 ml of distilled water. An intense red color depending on Sb(III) concentration is observed in the chloroform layer. Better separation of the layers can be achieved by addition of water or by centrifugation for 10 seconds.

As little as 0.05µg Sb(III) can be detected particularly when the reaction is compared with a blank.

Limit of identification: 0.05µg Sb(III).

Limit of dilution: 1:1,000,000.

Reagents: 0.4% reagent in chloroform.
0.3 N HCl.
Chloroform.

3.- Effect of Reagent on Other Cations

The following table, Table 5 shows the colors obtained when the procedure described above is applied to various cations. In each case a drop of the test solution containing 500μg of the cation is used.

Table 5

Colors Obtained with Various Cations

Ions	Color Obtained	Ions	Color Obtained
Li(I)	yellow	Th(II)	yellow
Na(I)	yellow	V(V)	red in water
K(I)	yellow	Cr(III)	yellow
Rb(I)	yellow	Mo(VI)	yellow
Cs(I)	yellow	W(VI)	yellow
Be(II)	yellow	U(VI)	red
Mg(II)	yellow	Mn(II)	yellow
Ca(II)	pink	Fe(III)	yellow
Sr(II)	yellow	Co(II)	yellow
Ba(II)	yellow	Rh(II)	yellow
La(III)	yellow	Ni(II)	yellow
Ce(III)	yellow	Pd(II)	yellow
Ce(IV)	yellow	Pt(IV)	yellow
Zr(IV)	yellow	Cu(II)	yellow

Table 5 - continued

Ions	Color Obtained	Ions	Color Obtained
Ag(I)	yellow	Tl(I)	yellow
Au(III)	orange	Sn(II)	yellow
Zn(II)	yellow	Sn(IV)	yellow
Cd(II)	yellow	Pb(II)	yellow
Hg(I)	yellow	As(III)	yellow
Hg(II)	yellow	As(V)	yellow
Al(III)	yellow	Bi(III)	red
		Sb(V)	yellow

The results clearly show that the interfering cations are U(VI), Bi(III) and Au(III), The other cations produce a yellow color distinguishing them from the red Sb(III) chelate. The color of V(V) is of no consequence since it is not extracted in chloroform.

The reagent does not react with antimony (V). This was confirmed by a number of tests carried on compounds of Sb(V). Further, Sb(III) oxidized to Sb(V) with hydrogen peroxide fails to give a test.

4.- Effect of Reagent on Anions

To test for the effect of the various anions (1% solutions) on the antimony test, two sets of experiments were carried out. In the first set, a drop of each of the anion solutions was treated as in the procedure described above. In the second set the procedure was repeated in the presence of 0.5µg antimony.

The results are summarized in Table 6. Whenver 0.5µg antimony failed to give a positive test, the concentration of the antimony was increased until a test was obtained. The concentration of antimony is indicated in between brackets.

Table 6

Colors Obtained with Anions

Anions	Anions alone	Anions + Sb(III)
F^-	yellow	red
Cl^-	yellow	red
Br^-	yellow	red
I^-	yellow	red
NO_3^-	yellow	red
$SO_4^=$	yellow	red
$S^=$	yellow	red (50µg)
$S_2O_3^=$	yellow	red
CN^-	yellow	red
$CO_3^=$	yellow	red
$PO_4^{\equiv}$	yellow	red

Table 6 - continued

Anions	Anions alone	Anions +Sb(III)
Citrate	yellow	red
Tartrate	yellow	red
Malonate	yellow	red
EDTA	yellow	red
CNS^-	yellow	red
$CrO_4^=$	yellow	red (5µg)
MnO_4^-	yellow	red (5µg)
Oxalate	yellow	red
S_2O_8	yellow	red (5µg)

5.- Detection of Sb(III) in the Presence of Foreign Cations

All experiments seemed to indicate a dependance of chelation on pH. The red color of Sb(III) chelate was not observed when 6 N HCl was added instead of 0.3 N. To find the appropriate pH at which the effect of interfering cations is removed, several buffers were tried. It appeared that a mixture of HCl and ammonium acetate gave the best result. A mixture of 1 part 6N HCl to three parts 9% ammonium acetate (pH 0.235) was found to be the most effective in removing the interference of U(VI) and Au(III). Bismuth however still interfered. Several attempts at masking bismuth failed; they all either completely masked antimony or appreciably decreased the sensitivity of the test. The buffer did not decrease the sensitivity of the Sb(III) test.

Of the various reagents tried to mask bismuth, thiourea seemed to be the most satisfactory. Addition of a drop of a saturated solution of thiourea gave an intense yellow complex with Bi(III) and a pale yellow complex with Sb(III) both of which were not extracted in chloroform. When the procedure described below was repeated with thiourea, bismuth was removed completely leaving Sb(III) relatively unaffected.

Procedure: Add 4 drops of the buffer solution to one drop of the test solution, then add 4 drops of the reagent in chloroform. The red color formed is extracted in chloroform. In the presence of bismuth add a drop of thiourea before the addition of the reagent.

Limit of identification: 0.05μg Sb(III).

Limit of dilution: 1:1,000,000.

Reagents: 0.4% reagent in chloroform.

Buffer solution.

Chloroform.

Saturated solution of thiourea in water.

The procedure described above was applied to the cations listed in Table 1. None of the cations interfered by giving a color in the chloroform layer. The mixture of 6N HCl and 9% ammonium acetate was therefore adopted to control the pH and thiourea to remove the interference of bismuth.

6.- Limits of Identification of Sb(III) in the Presence Foreign Ions

The work described above has shown that the buffer did not affect the identification limit of the antimony test which remained at 0.05µg. It was therefore desirable to determine quantitatively the sensitivity of the antimony test in the presence of foreign ions. For this purpose, experiments were carried where the procedure described above was applied. In all cases the concentration of the foreign ion was maintained at 500µg while the concentration of antimony was decreased until the limit of identification could be clearly determined. Results are shown in Table 7.

Table 7

Limits of Identification of Sb(III) in the Presence of Foreign Cations

Cations	Limits in µg	Cations	Limits in µg
Li(I)	0.1	Cs(I)	0.1
Na(I)	0.1	Be(II)	0.1
K(I)	0.1	Mg(II)	0.1
Rb(I)	0.1	Ca(II)	0.1

Table 7 - continued

Cations	Limits in μg	Cations	Limits in μg
Sr(II)	0.1	Pd(II)	0.1
Ba(II)	0.1	Pt(IV)	0.1
La(III)	0.1	Cu(II)	0.1
Ce(III)	0.1	Ag(I)	0.1
Ce(IV)	0.5	Au(III)	0.5
Zr(IV)	0.1	Zn(II)	0.1
Th(II)	0.1	Cd(II)	0.1
V(V)	0.5	Hg(I)	0.5
Cr(III)	0.1	Hg(II)	0.1
Mo(IV)	0.1	Al(III)	0.1
W(VI)	0.1	Tl(I)	0.1
U(VI)	0.2	Sn(II)	0.1
Mn(II)	0.1	Sn(IV)	0.1
Fe(III)	0.1	Pb(II)	0.5
Co(II)	0.1	As(III)	0.1
Rh(II)	0.1	As(V)	0.1
Ni(II)	0.1	Bi(III)*	0.5

* Bi(III) test was done with 1 drop saturated thiourea.

7.- Detection of Sb(III) in Mixtures of Foreign Cations

In the following set of experiments Sb(III) was detected in nine different solutions each containing at least five cations. Standard solutions containing 1% of the cation are prepared (i.e. 500μg per drop). Take one drop from each solution and mix in a test tube. Add ten drops of glacial acetic acid and 5 drops of thiourea to each mixture and shake well, and follow this with 10 drops of the reagent. Observe the color in the chloroform layer. The same procedure is applied to mixtures containing the same cations and one drop of 1% Sb(III). The results of these experiments are summarized in Table 8.

Table 8

Detection of Antimony in Various Mixtures

Mixtures of Ions	Color
Cu(II)+Co(II)+Mn(II)+Ni+Fe(III)	yellow
Cu(II)+Co(II)+Mn(II)+Ni+Fe(III)+Sb(III)	red
Zn+Ba+Tl(I)+Sr+Ca+Al	yellow
Zn+Ba+Tl(I)+Sr+Ca+Al+Sb(III)	red
Li+W(VI)+Pb(II)+K+Hg(II)	yellow
Li+W(VI)+Pb(II)+K+Hg(II)+Sb(III)	red
Cr(III)+Hg(I)+Zr(IV)+Mg+As(V)+Pd(II)	yellow
Cr(III)+Hg(I)+Zr(IV)+Mg+As(V)+Pd(II)+Sb(III)	red
V(V)+Au(III)+Na+U(VI)+Ce(IV)+Ag(I)	yellow
V(V)+Au(III)+Na+U(VI)+Ce(IV)+Ag(I)+Sb(III)	red

Table 8 - continued

Mixtures of Ions	Color
Cd+Sn(II)+Sn(IV)+As(III)+Pt(IV)	yellow
Cd+Sn(II)+Sn(IV)+As(III)+Pt(IV)+Sb(III)	red
Th(II)+Cs+Be+La(III)+Rb+Rh(II)+Ce(III)	yellow
Th(II)+Cs+Be+La(III)+Rb+Rh(II)+Ce(III)+Sb(III)	red
U(VI)+Ce(IV)+Au(III)+Sn(II)+Sn(IV)	yellow
U(VI)+Ce(IV)+Au(III)+Sn(II)+Sn(IV)+Sb(III)	red

A similar experiment was also carried out in the presence of bismuth, with one drop of saturated thiourea

U(VI)+Ce(III)+Au(III)+Sn(II)+Bi	yellow
U(VI)+Ce(III)+Au(III)+Sn(II)+Bi+Sb(III)	red

The procedure described above was finally tested by detecting Sb(III) in a solution containing all the cations listed in Table 1. This solution was prepared by taking a drop from each cation mixed with 5 drops of 1% Sb(III). The procedure adopted is the following: To the mixture add 20 drops of buffer, 1 drop of saturated thiourea and 10 drops of the reagent.

Solution (i): Li + Na + K + Rb + Cs + Be + Mg + Ca +
Sr + Ba + Zr(IV) + V(V) + Cr(III) + Mo(VI)
W(VI) + Mn(II) + Fe(III) + Co(II) + Ni +
Pd(II) + Pt(IV) + Cu(II) + Ag + Au(III) +

Zn + Cd + Hg(I) + Hg(II) + Al + Tl(I) + Sn(II) + Sn(IV) + Pb(II) + As(III) + As(V) + U(VI) + Bi + La(III) + Ce(III) + Ce(IV) + Th(II) + Rh(II).

Solution (2): Solution (1) + Sb(III).

Results: Solution (2) produced a red color while solution (1) gave a yellow color.

It was also possible to detect Sb(III) in the pharmaceutical product, tartar emetic.

These results are highly satisfactory and show that the procedure is functional and can be applied for the detection of Sb(III) in the presence of a very large number of foreign ions.

PART THREE: BISMUTH TEST

A. Historical:

The literature is quite rich in tests for bismuth, most of which are based on precipitation. However, detection by reduction to metallic bismuth and complex formation reactions are also used.

Filter paper impregnated with cinchonine gives an orange red fleck in the presence of potassium iodide when a slightly acidic solution of bismuth having a concentration greater than 0.14μg is added. Hg(II), Pb(II) and Cu(II) interfere; a preliminary removal of these ions is therefore necessary, appreciably reducing the sensitivity of the test (52). Other organic bases, such as alcoholic solution of quinoline, also give an orange red color in the presence of KI. The identification limit is 1μg bismuth. Here again Pb(II), Sb(III), Hg(I), Ag, Cu(II) and Fe(III) interfere (53).

A yellow color, with an identification limit of 1μg is produced by extraction of the bismuth iodide with isobutyl ketone. Platinum and palladium interfere (54).

Tomicka reports several methods for the detection of bismuth. Bismuth can be spot tested on filter paper impregnated with a mixture of KI, caprolactam and sodium hypophosphate at concentrations greater than 0.03µg. Cu(II) and Sb(V) interfere by delaying the reaction(55). In a second procedure a mixture of BiI_4^- in nitric acid reacts with caprolactam and is detected and determined at 420µm after extraction with chloroform and acetone. Hg(II), Sb(III) and Cl^- interfere with the test (56). A one per cent solution of thiocaprolactam in chloroform is also used to detect bismuth on chromatographic paper with a limit of identification of 0.4µg. Addition of KI increases the sensitivity to 0.04µg (57).

Korenman and co-workers (37) have reported another procedure to detect bismuth using KI. In the presence of $Pb(NO_3)_2$ and Na_2S, addition of KI to the test solution acidified with nitric acid, results in a yellow-brown precipitate with a limit of identification of 0.1µg bismuth in 5 ml solution. This test is quite specific except for a slight interference from Au(III) (1µg in 250µg Au). Other inorganic reagents used to precipitate bismuth are: ammonium thiocyanate, to detect bismuth in minerals by forming yellow $Bi(CNS)_3$ (58); $K_3[Cr(CNS)_6]$, to give brick red $Bi[Cr(CNS)_6]$ precipitate at bismuth concentrations up to 0.4µg. However Hg(II), Ag, Tl(I) and Pb(II) interfere giving pink or yellow precipitates (59).

1,3[bis(8-mercapto-7-thiophyllinyl)] propane is another reagent which gives a red precipitate with bismuth salts in hydrochloric acid solution. This test has a sensitivity of 50μg/0.05 ml (60).

At the appropriate pH, isonaphtazarine (61) and 3-aminolawsone (62) precipitate bismuth selectively, but both reagents precipitate heavy metal ions in acidic and basic media, and hence special pH control is essential.

4-mercapto resorcinol (63), thiopyrogallol (64), mercapto and thiosemicarbazone derivative of thiazole carboxaldehyde (65), thiosemicarbazone derivative of 4,4'bithiazole (66), sodium salt of m-sulfanilamide benzoic acid (67) are also used to precipitate bismuth. However, due to lack of sensitivity and specificity, none of these reagents is very useful for the detection of bismuth.

Hematoxylin at pH 1-3 forms a violet complex with bismuth at concentrations above 5μg/ml. The complex is decomposed by EDTA. Al, Fe(III) and Hg(II) interfere. A filter paper procedure utilizing ascorbic acid to remove the interference of Fe(III) and Hg(II) is adopted. This raises the limit to 0.1μg/0.05 ml (68).

Alkaline stannite solution reduces bismuth salts and bismuth hydroxide to metallic bismuth. The limit of identification is 1μg (69). In the presence of $Pb(NO_3)_2$ the reaction is more sensitive with a limit of identification of 0.01μg (70). Hg(II) and Cu(II) interfere, and special procedures should be adopted. A specific reducing agent is $K_4[Mn(CN)_6]$ which reduces bismuth to BiO. However, the sensitivity is 10μg Bi in 0.01 ml (71).

B. Experimental:

1.- Preparation of the Reagent

The preparation of the reagent solution is similar to that for the antimony test.

2.- Detection of Bismuth

Use the same procedure as for antimony.

Limit of identification: 0.5μg bismuth.

Limit of dilution: 1:100,000

3.- Effect of Reagent on other Cations

Same as for antimony.

4.- Effect of Reagent on Anions

Same as for antimony.

5.- Detection of Bismuth in the Presence of Foreign Cations

Same as for antimony. When antimony is present its interfering effect is removed by oxidation to Sb(V) since in this state of oxidation it does not react with the reagent.

Procedure: To a drop of the test solution add 2 drops of 15% hydrogen peroxide and heat in a water bath for about one minute, add 4 drops of buffer solution followed by 4 drops of 0.4% reagent in chloroform and observe color in chloroform layer.

Limit of identification: 0.5μg. of bismuth

Limit of dilution: 1:100,000

Reagents: 0.4% reagent in chloroform.
Buffer solution.
15% hydrogen peroxide.

6.- Limits of Identification of Bismuth in the Presence of Foreign Cations

The limit of identification of bismuth, in the presence of each cations was 10 times its corresponding value with antimony.(see Table 7).

7.- Detection of Bi(III) in Mixtures of Foreign Ions

The cation mixtures and the procedure used to detect Bi(III) in mixtures were similar to that for antimony. The results are summarized in Table 9.

Table 9

Detection of Bismuth in Various Mixtures

Mixtures of Ions	Color
Cu(II)+Co(II)+Mn(II)+Ni+Fe(III)	yellow
Cu(II)+Co(II)+Mn(II)+Ni+Fe(III)+Bi	red
Zn+Ba+Tl(I)+Sr+Ca+Al	yellow
Zn+Ba+Tl(I)+Sr+Ca+Al+Bi	red
Li+W(VI)+Pb(II)+K+Hg(II)	yellow
Li+W(VI)+Pb(II)+K+Hg(II)+Bi	red
Cr(III)+Hg(I)+Zr(IV)+Mg+As(V)+Pd(II)+	yellow
Cr(III)+Hg(I)+Zr(IV)+Mg+As(V)+Pd(II)+Bi	red
V(V)+Au(III)+Na+U(VI)+Ce(IV)+Ag(I)	yellow
V(V)+Au(III)+Na+U(VI)+Ce(IV)+Ag(I)+Bi	red
Cd+Sn(II)+Sn(IV)+As(III)+Pt(IV)	yellow
Cd+Sn(II)+Sn(IV)+As(III)+Pt(IV)+Bi	red
Th(II)+Cs+Be+La(III)+Rb+Rh(II)+Ce(III)	yellow
Th(II)+Cs+Be+La(III)+Rb+Rh(II)+Ce(III)+Bi	red
U(VI)+Ce(IV)+Au(III)+Sn(II)+Sn(IV)	yellow
U(VI)+Ce(IV)+Au(III)+Sn(II)+Sn(IV)+Bi	red

A similar experiment was also carried out in the presence of antimony, after oxidation with 15% hydrogen peroxide.

U(VI)+Ce(III)+Au(III)+Sn(II)+Sb(III)	yellow
U(VI)+Ce(III)+Au(III)+Sn(II)+Sb(III)+Bi	red

The procedure was finally tested by detecting Bi(III) in a solution containing all the cations listed in Table 1. This solution was prepared by taking a drop from each cation mixed with 5 drops of 1% Bi(III). The procedure adopted is the following: To the mixture add 20 drops of buffer 2 drops of 15% hydrogen peroxide and heat. Add 10 drops of the reagent.

Solution (I): Li+Na+ K + Rb + Cs + Be + Mg + Ca + Sr
Ba + Zr(IV) + V(V) + Cr(III) + Mo(VI)
W(VI) + Mn(II) + Fe(III) +Co(II) + Ni +
Pd(II) + Pt(IV) + Cu(II) +Ag + Au(III) +
Zn + Cd + Hg(I) + Hg(II) + Al + Tl(I) +
Sn(II) + Sn(IV) + Pb(II) + As(III) + As(V)
+ U(VI) + Sb(III) + La(III) + Ce(III) +
Ce(IV) + Th(II) + Rh(II).

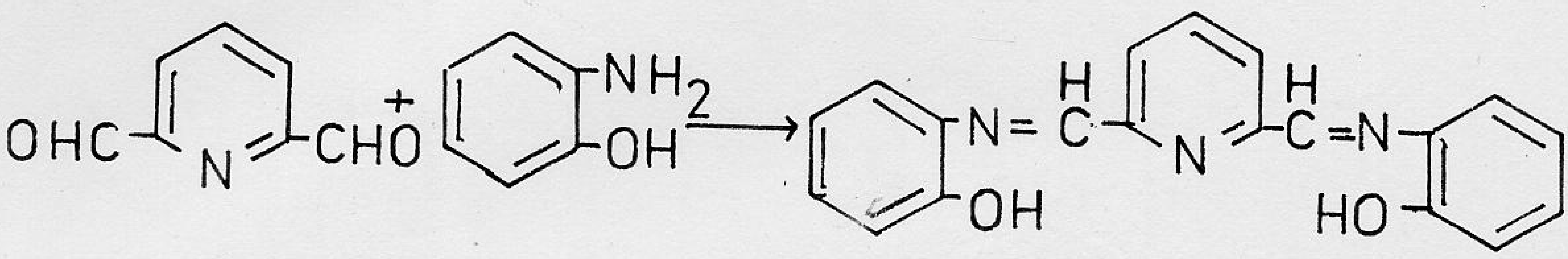
Solution (2): Solution (1) + Bi.

It was also possible to detect bismuth in the pharmaceutical product, Bismuth Tulasne, using the above procedure.

CHAPTER III

DISCUSSION

The condensation of 2,6-pyridine dicarboxaldehyde with o-aminophenol forms the following Schiff base (I).

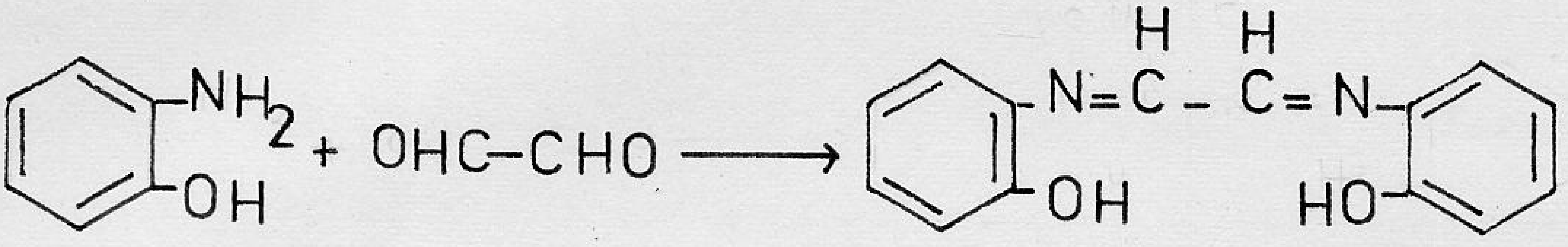


(I)

In the absence of a study of the nature of the complex formed in solution with uranium, antimony and bismuth, and its empirical formula it is difficult, at this stage, to postulate a definite structure for the complexes.

Study of the atomic models of the Schiff base show that it is planar. It is doubtful that a rigorously flat polydentate ligand can satisfy the stereochemical requirements of such a variety of metals as Cu(II), Ni, Mn(II), Zn, Pb, Cd(II), Tl(I), Mg(II), Co(II), Fe(III), Cr(III), Th(IV) all of which form red complexes with the reagent in alkaline medium (72).

The stability of the complexes obtained in acid medium is unusual, the vast majority of colored chelates being formed in alkaline medium when the hydrogen ions may be stripped from the phenolic groups. This is not unique, however, since Bayer (11) had reported that U(VI) formed red complexes with glyoxal bis(o-hydroxyanil), a Schiff base obtained from the condensation of glyoxal and o-aminophenol (II).

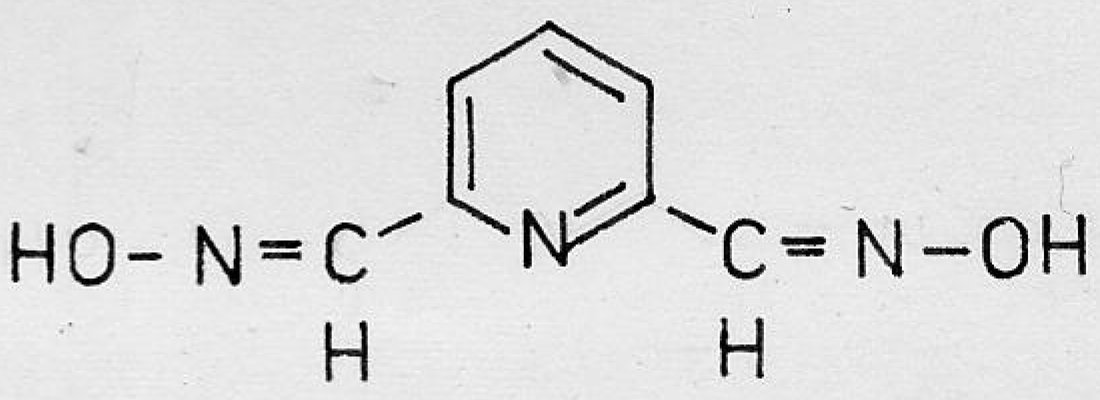


(II)

In fact, it appears that the arrangement of the coordinating and donor groups in Schiff base (I) is identical to that in Schiff base (II) except that the former has an additional center of coordination: the pyridine nitrogen.

The fact that more intense and more stable colors are obtained with (I) than with (II) is no doubt due to the increased resonance and to the heavier molecular weight which contributes a weighting factor.

There is strong evidence that the two phenolic groups in (I) are acting as a center of coordination even in acidic medium. Thus when 2,6-pyridine dialdehyde is condensed with aniline a Schiff base similar to (I) is obtained but without the two phenolic groups. This Schiff base does not form colored chelates with U(VI), Bi(III) or Sb(III). It would seem that salt formation takes place by phenolic hydrogen replacement even in acidic medium. There would seem to be a competition between the metal ion and the hydrogen ion for the phenolic oxygen. That the metal-oxygen bond (particularly uranyl) is stronger than the hydrogen-oxygen bond is substantiated by the fact that once the red chelate is formed it will not be decomposed even by the addition of excess acid. The role of the hydroxyl groups acting as coordination centers is also demomstrated by the fact that 2,6-pyridine dialdoxime (III)



(III)

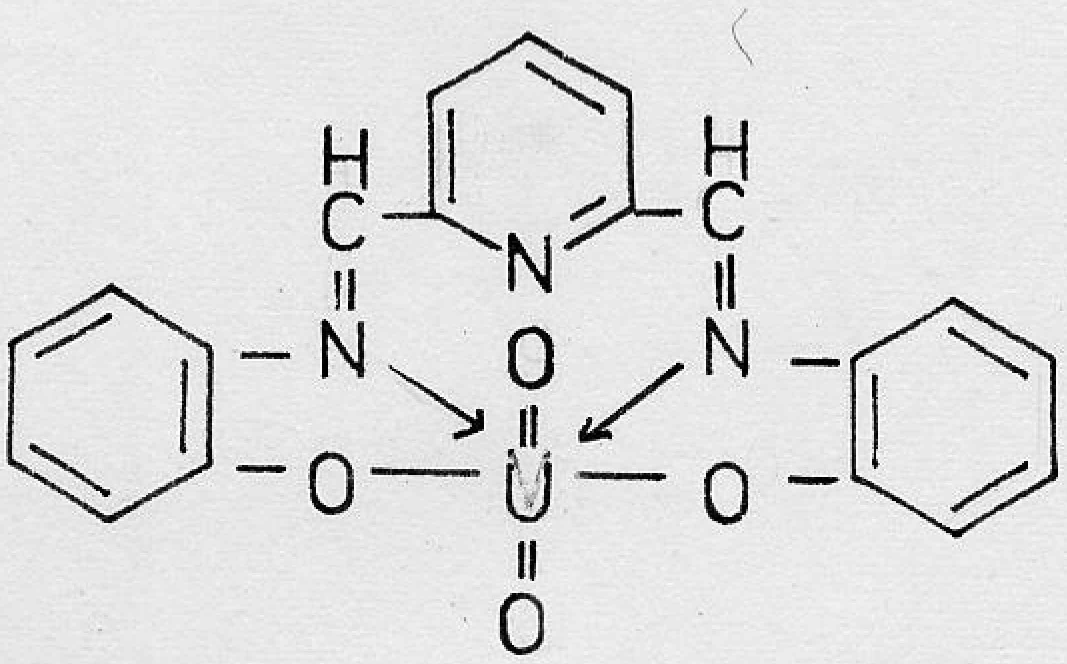
which has essentially the same structure as the reagent (I) except for the position of the hydroxyl groups does not form colored chelates with uranium, antimony and bismuth.

There remains the question of why these chelates are decomposed in alkaline solution when they should have been more stable. An examination of the ions that give intensely colored chelates in acid medium shows that these are U(VI), Sb(III) and Bi(III). At such pH ranges all these exist as condensed ions of the type UO_2^{++}, $BiOH^{++}$, BiO^{+}, $Bi_2O_4^{++}$, BiO_2^{+5}, SbO^{+} etc. When the solution is made alkaline, the hydroxyl ions are picked by the cations preferentially to give insoluble hydroxides and the corresponding uranate, antimonate and bismuthate which will not coordinate with the chelating agent.

That this is so is confirmed by the fact that vanadyl ions, VO_2^{+}, give with the reagent a red color. The test does not interfere since the color is not extracted in chloroform. Molybdenum which also forms condensed ions in acidic medium should therefore have also formed a red color with the reagent. No such reaction was however observed; this could be due to the fact that with molybdenum, these condensed ions are only formed in very acidic solutions when the chelate is decomposed or not formed at all.

On this basis and keeping in mind the fact that the chelating agent is a flat molecule it becomes possible to suggest a mechanism for the chelation.

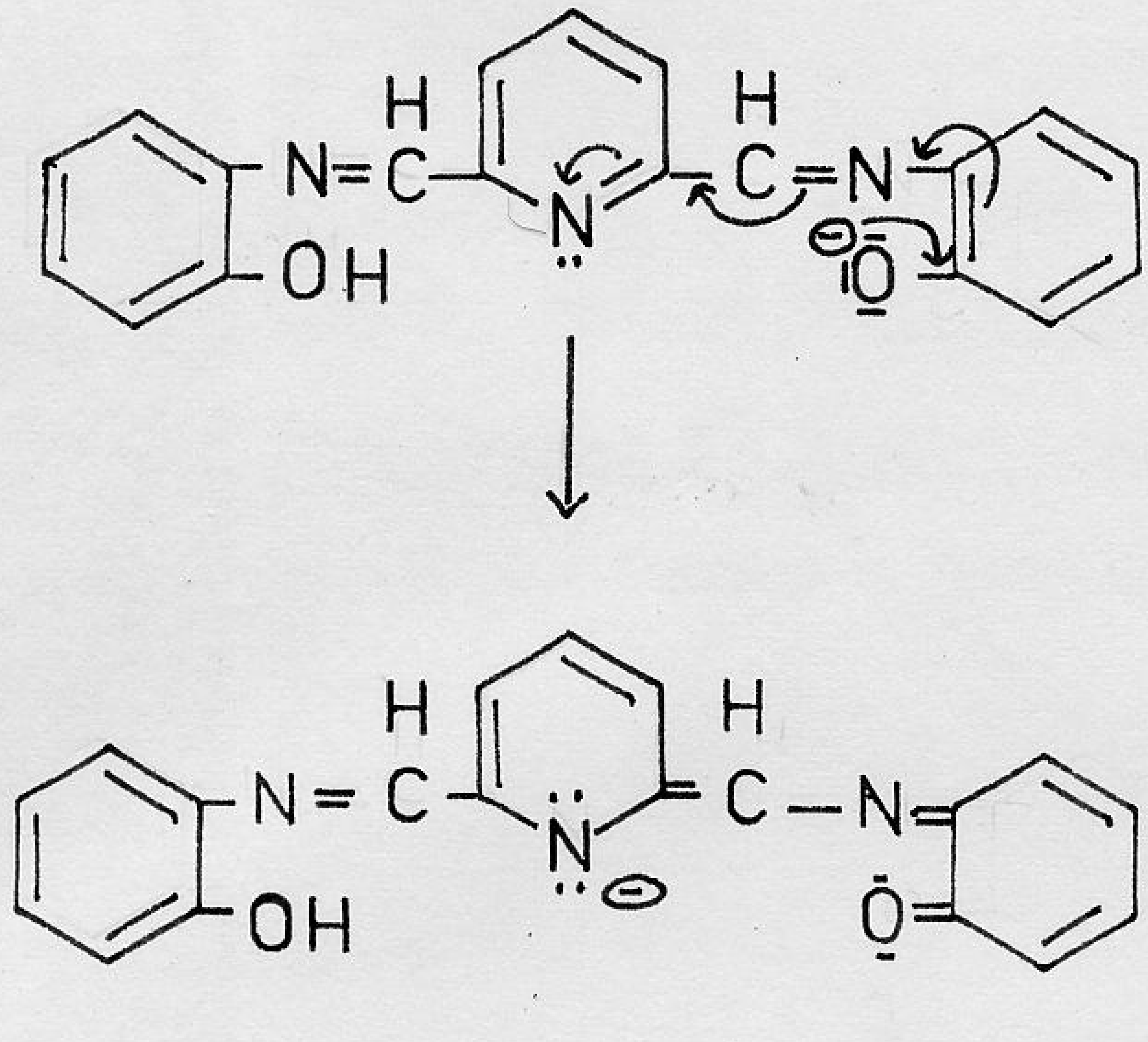
For the uranyl ion for instance the chelate will be as shown in (IV)



(IV)

Such an arrangement will satisfy the stereochemical requirements of uranium, antimony and bismuth. It is difficult otherwise to see how three molecules of the Schiff base can surround the metal ion; steric hindrance would not permit it. The oxygenated condensed ions will have four vacant positions in a plane which will be satisfied by the four planar coordination positions of the chelating agent.

Such a spatial arrangement would satisfy the coordination requirements of the ions that react with the Schiff base; it could also provide an explanation for the red colors obtained when chelates are formed. That all colored chelates should be red is an indication that this color is not due to the bonds formed between the metal and the chelating agent only but also to the resonance which arises when the chelate is formed. This is shown below in (V).



(V)

The quinoid structure and the extended conjugate system could thus be responsible for the red colors obtained.

BIBLIOGRAPHY

1. Bayer, E. Angew. Chem., 3, 325,(1964).
2. Jungreis, E. and S. Thabet, "Analytical Application of Schiff Bases," Chelates in Analytical Chemistry, edited by H. Flaschka and A. Barnard, publisher, Marcel Dekker, New York (in press).
3. Papadapoulos, E.P., A. Jarrar and C.H. Issidorides, J. Organic Chem., 31, 615 (1966).
4. Bartolome, M.L.A. Rev. Fac. Cienc. Univ. Oviedo, 5, 5-88 (CA 61, 11310d).
5. Van Ligten, J.W.L. and W. Cool. Anal. Chim. Acta, 29, 89-92 (1963).
6. Feigl, F. Spot Tests in Inorganic Analysis, Elsevier Publishing Co., New York, 5th ed., 1958, p. 205.
7. Sergorskaya, V.V. Tr. Ural'sk Politekhn. Inst. 1962, 63-66 (CA 59, 12177h).
8. Feigl, F. Spot Tests in Inorganic Analysis, Elsevier Publishing Co., New York, 5th ed., 1958, p. 204.
9. Liimatta, A.M. and J.D. Spain. Anal. Chem., 35, 1898-1900, (1963).
10. Pavlovskaya, M.P. and I.M. Reibel. Tr. Kishinevsk. sel's kokhoz inst., 1962, 58-63. (CA 59, 6991h).
11. Bayer, E. Ber., 90, 2325, (1959).
12. Bayer, E. and H. Mollinger, Angew. Chem., 71, 426, (1959).

13. Feigl, F. *Spot Tests in Inorganic Analysis*, Elsevier Publishing Co., New York, 5th ed., 1958, p. 208.

14. ibid., p.209.

15. ibid., p.207.

16. ibid., p.210.

17. ibid., p.207.

18. Jungreis, E. and L. Ben Dor. *Anal. Chim. Acta*. *30*, 405-7, (1964).

19. Feigl, F. Spot Tests in Inorganic Analysis, Elsevier Publishing Co., New York, 5th ed., 1958, p. 209,210.

20. Buscarons, F. and J. Abello. *Anales Real Soc. Espan. Fis. Quim. Ser. B.* *58*, 591-600. (CA 58, 9611h).

21. Berg, E.W. and A. Alam. *Anal. Chim. Acta*. 27, 454-9, (1962).

22. Mary, L.G. and S.L. Srivastava. *Talanta*, *12*, 181-3, (1965).

23. Tserkarevich, K.V. and N.S. Polvetkov. *Zh. Analit. Khim*. *19*, 1309-14, (1964) (CA 62, 7106c).

24. Kashkovskaya, E.A. and I.S. Mustafin. *Trudy Komissii Anal. Khim. Akad. Nauk USSR Inst. Geokhim. i Anal. Khim*. *11*, 97-112, (1960). (CA 55, 9162g).

25. Berger, W. and H. Elvers. Z. Anal. Chem. 171, 185-93, (1959).

26. Ryazanov, I.P. and I.P. Khazova. *Izvest Vysschikh Ucheb* Zavedenii Khim. i Khim. Tekhnol. 2, 490-2 (1959) (CA54,1183).

27. Sommer, L. *Z. Anal. Chem*. *187*, 263-74 (1962).

28. Ryazanov, I.P. and I.P. Khazova. *Sb. Nauck. Tr. Magnitogor Gornomet. Inst*. *1961*, No. 23, 92-7. (CA 57, 4002a).

29. Cherapakhin, A.I. *Vsesoyoz. Zaochnyi Politekh. Inst., Sbornik Statei*, 1960, No. 23, 47-55. (CA 56, 2872b).
30. Datta, S.K. *Chemist-Analyst*. 50, 104-5, (1961).
31. Feigl, F. *Spot Tests in Inorganic Analysis*, Elsevier Publishing Co., New York, 5th ed., 1958, p. 103-7.
32. ibid., p.103.
33. Henry, A.J. *Analyst*. 89, 242-54, (1964).
34. Vignoli, L.B., B. Cristan, and F. Gronezo. *Bull. Soc. Chim. France.* *1959*, 1892-4, (1959).
35. Cinhandu, Gh. and M. Rocsin. *Acad. rep. Populaire Romine studii cercatari Chim*. *8*, 537-9, (1960) (CA 55, 9162d).
36. Feigl, F. *Spot Tests in Inorganic Analysis*, Elsevier Publishing Co., New York, 5th ed., 1958, p. 104.
37. Korenman, I.M., F.I. Leifer, and S.F. Solov'ena. *Trudy* Khim. i Khim. Tekhnol. 2, 112-114 (1956) (CA, 54, 10657).
38. Rouf, A., and S.S.M.A. Khorassani, *Sci. Res*. *2*, 40-2,(1965).
39. Adamovich, L.P. Ukr. Khim. Zh. 27, 817-23 (CA 56, 14a).
40. Levin, A.B. *Trudy Ural. Politikh. Inst. im S.M. Kirova, 1960*, No. 94, 106-9 (CA 56, 12295b).
41. Jimeno, S.A. and M.L. Alvarez. *Bartolome Univ. Oviedo Rev. Fac. Cienc*. 3, No. 2, 509, (1962) (CA 58, 13108h).
42. Bagbanly, L.L. *Izvest. Akad. Nauk Azerbaidzhan S.S.R*. *24*, 528-31, (1958) (CA 54, 11829d).
43. Feigl, F. *Spot Tests in Inorganic Analysis*, Elsevier Publishing Co., New York, 5th ed., 1958, p. 105.

44. Fujimoto, M. and T. Iwamoto. *Mikorchima. Ichnoanal. Acta. 1963*, 655-67. (CA 60, 13858f)

45. Dunbar, R.E. and F.J. Ferrin. *Michrochem. J.* 5, 145-57, (1961) (CA 61, 1244c).

46. Khalutina, K.A., L. Tantsogreva, A. Sergaeva and M. Potyledyna. *Tr. Sibirsk. Tekhnol. Inst*. No. *36*, 87-93, (1963). (CA 62, 3381e).

47. Tewar, S.N. *Z. Anal. Chem*. *180*, 109-110. (1961).

48. Feigl, F., A. Caldas., L.S. Farsos de Azevdo. *Chemist Analyst*. *54*, 106-7, (1965).

49. Hemmeter, A. E. *Boni Studi Urbinati Fac. Farm*. *30*, 18-23, 24-32, (1956) (CA54, 22144).

50. Feigl, F. *Spot Tests in Inorganic Analysis*, Elsevier Publishing Co., New York, 5th ed., 1958, p. 107.

51. Stolyarov, K.P. and N.N. Grigariev. *Vestrick Leningrad Univ*. 14, No. 22, *Ser. Fiz i Khim*. No. 4, 104-11, (1959). (CA 54, 8435i).

52. Feigl, F. *Spot Tests in Inorganic Analysis*, Elsevier Publishing Co., New York, 5th ed., 1958, p. 76.

53. ibid., p.80.

54, ibid., p.80.

55. Tomicka, H.S. *Raczniki Akad. Med. im Juliana Marchlews* Kiego w Bialymstoku. 2, 1950201, (1956) (CA 56, 5388c).

56. Tomicka, H.S. *Z. Anal. Chem*. *187*, 258-62, (1962) (CA 56,

57. Tomicka, H.S. and K. Dzerepko. *Mikrochim. Ichnoanal. Acta*. **1964**, 888-90, (CA 54, 10657b).

58. Ozhigov, K. *Tr. Dalnevost. Filiala. Akad. Nauk SSSR* Ser. Khim. 1961, 116-24 (CA 57,9197g).

59. Feigl, F. *Spot Tests in Inorganic Analysis*, Elsevier Publishing Co., New York, 5th ed., 1958, p. 79.

60. Stahle, H. *Deut. Apotheker ztg*. 100, 777-8, (1960). (CA 54, 21656f).

61. Nagase, Y. and U. Matsumoto. *Yakugaku Zasshi*. **81**, 622-626, (1961) (CA 55, 21962c).

62. ibid., p. 627-30. (CA 55, 21962d).

63. Buscarons, F. and J. Alsina. *Inform. Quim. Anal*. **19**, 12-22, (1965) (CA 62, 10645h).

64. Atsushi, S., M. Dan and Y. Kakasawa. *Bunseki Kagaku*. **13**, 1037-40, (1964) (CA 62, 1057e).

65. Uno, T. and S. Akihama. *Bunseki Kagaku*. **10**, 750-5, (1961) (58, 6167g).

66. ibid., p. 755-60.

67. Gnesin, Y.D. *Uchenye Zapiski. Pyatigorsk. Farm. Inst.* **4**, 107-16, (1969) (CA 56,6635d).

68. Mel'nikova, A.S.A. and S.N. Khramova. *Tr. Astrakhanst Tekhn. Inst. Rybn*. No. 8, 82-8, (1962) (CA 60, 2316f).

69. Feigl, F. *Spot Tests in Inorganic Analysis*, Elsevier Publishing Co., New York, 5th ed., 1958, p. 80.

70. ibid., p. 77.

71. ibid., p; 80.

72. Thabet, S. and D. Goldstein. unpublished studies.