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SEPARATION OF COPPER AND ARSENIC AND OF ARSENIC AND ANTIMONY**

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# COPRECIPITATION WITH FERRIC HYDROXIDE: AN APPLICATION TO THE SEPARATION OF COPPER AND ARSENIC AND OF ARSENIC AND ANTIMONY

M. B. A. Vasconcellos and F. W. Lima

## ABSTRACT

In this paper a method is presented for the chemical separation of the pairs copper-arsenic and arsenic-antimony by means of coprecipitation with ferric hydroxide. These pairs of elements are rather difficult to determine by activation analysis, due to the very close values of the energies of the gamma rays emitted by their radioisotopes obtained by thermal neutron activation. The efficiency of the separation is studied and the process is applied to the analysis, by activation, of artificial samples containing copper and arsenic and of a p.a. reagent,  $\text{FeCl}_3 \cdot 12\text{H}_2\text{O}$ . As for the pair arsenic-antimony, the separation only is studied, by determining the distribution of these two elements between the liquid and solid phases.

Copper is precipitated in solution by complexation with ammonium hydroxide and antimony by complexation with tartaric acid.

The distribution of the elements between the liquid and solid phases is followed by the counting of the activities of the radioisotopes copper-64, arsenic-76 and antimony-122.

Finally, the possibilities presented by the method of separation through coprecipitation for works at low concentrations are emphasized.

## 1 - INTRODUCTION

It is a well known fact that precipitates are not deposited completely free from impurities present in solution. By impurities we understand here chemical species other than the components of the precipitate.

The contamination of precipitates by the species present in solution can become a serious problem in gravimetric procedures and it is not always possible to eliminate the interfering ions.

In radiochemical work, on the other side, scavenging by precipitates is one the most frequently employed techniques for removing undesired impurities from solution or for concentrating elements present at trace levels. Since the fraction of removed impurity generally decreases with the increase of its concentration, it is a common procedure to add carriers of the elements that one wishes to keep in solution. The most commonly used scavengers in Radiochemistry are the colloidal precipitates of large surface area, such as ferric hydroxide, manganese dioxide, silver halides and sulfides of weakly electropositive metals.<sup>(1)</sup>

(1) From a Dissertation submitted by M. B. A. Vasconcellos to the Instituto de Química, University of São Paulo, in partial fulfillment of the requirements for a Master of Science Degree. Work supported by the Brazilian Atomic Energy Commission.

Even at low concentration, it is possible to avoid the carrying of certain elements by means of complexation or by controlling the pH of the solution. Several papers have been published, mainly by Russian researchers, in which radioactive isotopes of several elements, such as gold and thallium<sup>(10)</sup>, tantalum, tungsten and zirconium<sup>(11)</sup>, rare earths and hafnium<sup>(13)</sup>, tantalum and bismuth<sup>(12)</sup> are separated by coprecipitation with ferric hydroxide by changing the pH of the solution.

Studies on the coprecipitation of cations with ferric hydroxide precipitated with excess ammonia<sup>(16)</sup> showed that, in the case of elements like copper and zinc, which form soluble and stable ammoniacal complexes, the fraction carried decreases with the increase of ammonia concentration. This fact had already been observed by Kofthuff and Muskovitz<sup>(7)</sup>.

So it is that Uper and coworkers<sup>(17)</sup>, on studying the absorption by metal hydroxides of cations that form ammoniacal complexes, have determined the concentration of ammonium hydroxide and ammonium salts in which these cations are quantitatively kept in solution. This way, the complexed cations can be separated from the non-complexed ones.

One of the greatest obstacles to the success of instrumental neutron activation analysis using multichannel analyzers and NaI(Tl) scintillation counters is the occurrence of overlapping peaks of radioisotopes that emit gamma rays of very similar energies. This situation is illustrated for the pairs of radioisotopes copper-64 and arsenic-76, and of arsenic-76 and antimony-122, in Figures 1.1 and 1.2. When using high resolution solid-state gamma-ray Ge(Li) detectors it is possible to separate the peaks of copper and arsenic, but not always satisfactorily the ones of arsenic and antimony. When this occurs, it is necessary to resort to a chemical separation prior to counting.

Several papers have been published about the simultaneous neutron activation analysis of copper and arsenic and of arsenic and antimony or of all the three elements together. In many of these works, chemical separation methods are employed.

Grimanis<sup>(5)</sup> points out the importance of the simultaneous determination of copper and arsenic in wines and in biological samples, due to the significant role of copper as a trace element in the metabolism of living organisms and also to its influence in the taste of wines. In the case of arsenic, which is used as a pesticide in vines, there is always the possibility of its remaining as a toxic residue. The authors apply a solvent extraction technique to separate arsenic from copper.

Grimanis and Souliotis<sup>(16)</sup> have improved this technique and applied it to the rapid determination of arsenic and copper in brass samples.

Qureshi and collaborators<sup>(14)</sup> developed a process for the determination, by activation analysis, of copper, arsenic and antimony, using triethylenylamine as an extracting agent. The process was applied to the analysis of a lead alloy containing the three elements.

Dams and Hoste<sup>(2)</sup> have analyzed arsenic and antimony, besides selenium and tellurium, by neutron activation analysis, in electrolytic solutions of zinc sulfate. Arsenic and antimony were first precipitated as sulfides and then separated by distillation as chlorides.

Maenhaut and coworkers<sup>(9)</sup> have published a paper about the determination of arsenic and antimony in tin. After distillation in hydrobromic-sulfuric acids mean, arsenic and antimony were precipitated with thiocetamide and antimony was separated by deposition on iron powder.

Non-destructive neutron activation analysis was also used for the determination of arsenic and antimony, as in the work of Rudelli et al<sup>(15)</sup> in which the 0.657 MeV and 0.686 MeV secondary peaks of the radioisotopes arsenic-76 and antimony 122 were used for the analysis. High resolution Ge(Li) detector counting had to be employed.

Due to the frequent necessity of the radiochemical determination of the three mentioned

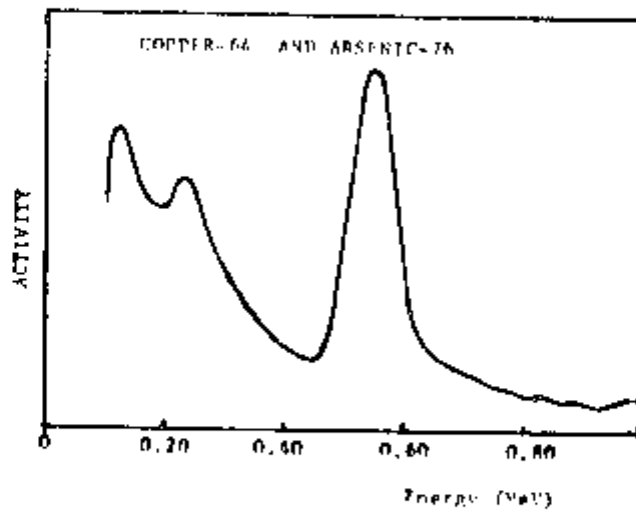
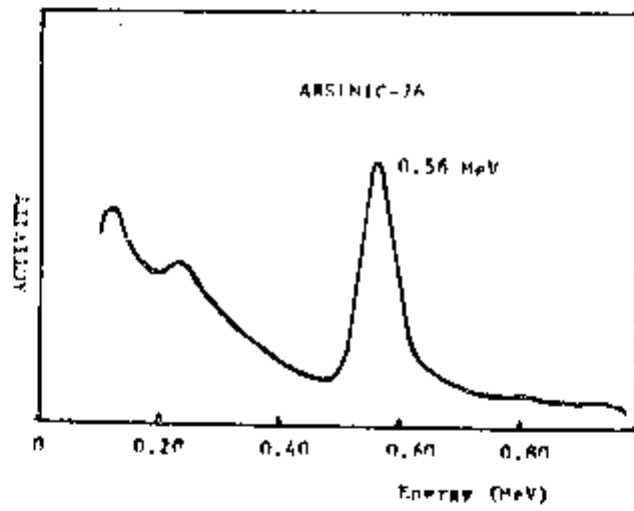
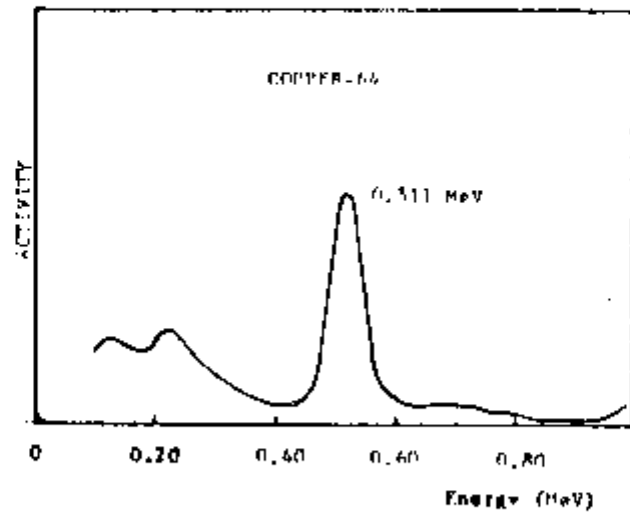


Figure 1.1 - Copper-64 and Arsenic-76 Spectra

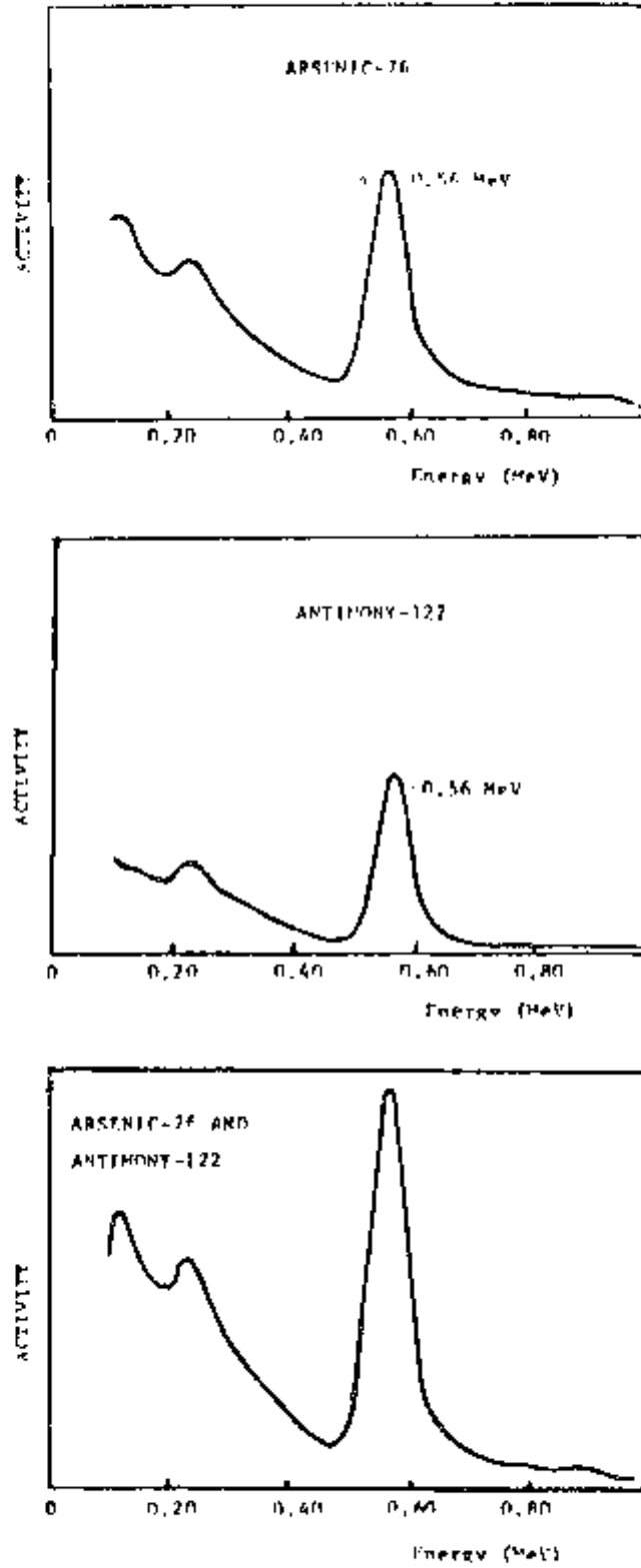


Figure 1.2 — Arsenic-76 and Antimony-122 Spectra



elements, that is, arsenic, antimony and copper and considering the fact that the gamma-ray energies of the corresponding radioisotopes are very close, which makes this simultaneous determination difficult, it was decided in the present work to study a chemical separation process which would be relatively rapid and sufficiently simple to allow the analysis of several samples at the same time.

Since copper has the property of forming soluble complexes with ammonium hydroxide it should not be coprecipitated with ferric hydroxide under certain experimental conditions. Arsenic and antimony, on the other side, should be carried down with iron hydroxide, giving a first separation and then a further change on pH or the increase of  $\text{NH}_3^+$  concentration could lead to the separation of the pair.

In the present work, the separation of copper and arsenic was first studied, considering the cases in which both elements are in trace concentration levels and in which copper is present in macroconcentrations and arsenic in microconcentrations.

Once the separation method was developed, copper and arsenic in trace levels were determined in a p.a. reagent,  $\text{FeCl}_3 \cdot n \text{H}_2\text{O}$ , by activation analysis.

The method was also applied to a sample of human hair that was put in contact with radioactive arsenic and copper. This determination can be required in cases of suspicion of arsenic poisoning. The amount of copper generally present in human hair, of about 30 to 50 ppm is enough to interfere with the direct analysis, with no chemical separation of arsenic, even in the cases where poisoning occurs, in which the proportion of this element is relatively large (100 to 200 ppm or even more).

The best solution found in this case for the separation of arsenic and antimony was the complexation of antimony with tartaric acid, since this reduces the carrying of antimony to levels lower than 15%, when ferric hydroxide is twice precipitated. The dependence between the coprecipitation and the concentration of tartaric acid was studied, since the coagulation of ferric hydroxide is hindered by an excess of tartaric acid.

The control of the fraction of the elements carried down by ferric hydroxide was made through the counting of the activities of the radioisotopes copper-64, arsenic-76 and antimony-122 of 12.8 hours, 26.4 hours and 2.68 days half-life, respectively. The counting of the activities was carried out by means of sodium iodide crystals, using mono or multichannel analyzers.

## II - EXPERIMENTAL PART

### II.1 - Reagents

The solutions used were all prepared with p.a. reagents, and were the following:

Copper nitrate solution

Ferric chloride solution

Ammonium hydroxide solution

Sodium borate buffer solution

Tartaric acid solution

## 11.2 - Irradiation

Copper was irradiated in the form of its nitrate solution, in quartz ampoules. The ampoules were placed in aluminum cans and irradiated for 8 hours in a neutron flux of about  $5 \times 10^{13}$  neutrons/cm<sup>2</sup> s.

Antimony was irradiated in the same form and by the same conditions as copper. The activated oxide was dissolved with 40% sodium hydroxide or with aqua regia and diluted to the desired concentration.

Antimony was irradiated in the metallic form and dissolved with aqua regia.

## 11.3 - Counting

The countings were carried out with the aid of sodium iodide crystals, coupled to mono- or multichannel analyzers.

The Nuclear Chicago monochannel analyzer, model 1820 A, coupled to a 5.1 x 4.4 cm well-type sodium iodide crystal was used when working with one active isotope only.

When working with more than one radioisotope, a TMC-402 multichannel analyzer coupled to a 5.1 x 4.4 cm well-type sodium iodide crystal was used.

The samples were counted in the liquid form, always looking that sample and standard had the same geometry in the counting tubes.

The counting time was of 10 minutes in general and the counting rate varied between  $10^3$  to  $10^5$  counts per minute, the most frequent counting rate being of  $10^4$  cpm.

The percentage of element in the liquid and solid phases was calculated by comparing the activity of each phase (or of an aliquot of this phase) to the initial activity present (or to a known fraction of this activity).

## 11.4 - Separation of Copper and Arsenic by Coprecipitation of Arsenic with Ferric Hydroxide

In the present work the possibility of the simultaneous determination by activation analysis of copper and arsenic was studied, using as separation method the coprecipitation with ferric hydroxide. The great advantages of this method are the speed and easiness of operation.

The experimental procedure described here for the separation of copper and arsenic is very similar to the one employed for the separation of arsenic and antimony.

The preliminary experiments were carried out using the radioactive isotopes separately, due to the overlapping of the peaks corresponding to the main gamma-ray energies of copper-64 and arsenic-76. The studies of coprecipitation were done by placing active copper in the presence of inactive arsenic and vice-versa. Once the separation conditions were established, the artificial samples used for analysis were prepared with both radioactive isotopes.

Solutions containing the two elements, active or not, were pipetted into 15 ml polypropylene centrifuge tubes, followed by adequate amounts of ammonium chloride and ammonium hydroxide solutions. Iron hydroxide was then precipitated by rapid addition of ferric chloride, at room temperature. This method leads to the formation of a precipitate of large surface area. After the precipitation, pH measurements were carried out, using a Philips PR 9400 pH meter, calibrated with a borax 0.01 M buffer solution.

After centrifugation for 10 minutes at 1600 rpm, aliquots of the supernatant liquid were pipetted into adequate counting tubes. For each sample series, a standard comparator solution was prepared, including all reagents except ferric chloride, which was substituted by an equal volume of water. With this procedure, the activity of the supernatant liquid of the samples could be directly compared to the activity of the standard.

As for the precipitates, after eliminating the supernatant liquid, the counting was made in the centrifuge tube itself. Only when the activity of the precipitate was too high its dissolution in nitric or hydrochloric acid became necessary and aliquots of this solution were taken for counting.

#### II.4.1 — Study of the Separation Conditions

The results of the first experiments carried out with active copper in the presence of inactive arsenic are in Table II.1. The experimental conditions were in this case very similar to the ones utilized by Uper<sup>(17)</sup> to obtain a minimum carrying of copper.

Table II.1  
Distribution of Copper in the Form of Ammoniacal Complex  
Between the Liquid Phase and the Precipitate

In the Liquid	% COPPER		In the Liquid	MASS OF COPPER (mg)	
	In the precipitate			In the precipitate	
	No washing	Washing with water		No washing	Washing with water
96.6	6.5	5.5	9.7	0.6	0.5
96.6	9.1	7.0	9.7	0.9	0.7
98.8	9.8	7.6	9.8	1.0	0.8
98.3	8.4	—	9.8	—	—
98.1	8.0	—	9.8	—	—

#### Experimental Conditions

Mass of copper	10 mg	NH <sub>4</sub> Cl concentration	= 1.2 M
Mass of arsenic	0.35 µg	pH	= 9.3
Mass of iron	= 9.6 mg	Final volume	= 10 ml
NH <sub>4</sub> concentration	= 1.5 M		

The distribution of arsenic between the liquid and solid phases was also studied in the same conditions, using arsenic-76 as tracer. The results are presented in Table II.2.

Table II.2

Distribution of Arsenic Between the Liquid Phase and the Precipitate

% ARSENIC			MASS OF ARSENIC ( $\mu\text{g}$ )		
In the Liquid	In the precipitate		In the Liquid	In the precipitate	
	No washing	Washing with water		No washing	Washing with water
0.8	103.8	95.5	0.0027	0.36	0.33
0.8	99.2	96.3	0.0029	0.35	0.34
0.8	101.2	97.5	0.0029	0.35	0.33
1.0	104.6	—	0.0035	0.37	—
0.9	103.4	—	0.0030	0.36	—

Experimental conditions: the same as mentioned in Table II.1

Even considering that most part (over 96%) of the copper initially present in the solution is not carried down by the ferric hydroxide precipitate and that the contrary occurs with arsenic, it is still not possible to determine arsenic in the presence of copper with the mass relationship used. That is the case in which arsenic appears as an impurity in a copper matrix. The area corresponding to the 0.56 MeV peak of arsenic-76 is about 1000 times less than the area of the 0.511 MeV annihilation peak of copper-64.

Another series of experiments was then carried out, using a higher concentration of ammonium hydroxide, to keep a still higher fraction of the copper ammoniacal complex in the supernatant liquid. The results are shown in Table II.3. Even so, the mass of copper that remains in the precipitate is enough to interfere with arsenic determination, because the area of the 0.511 MeV peak is 54 times that of the 0.56 MeV peak of arsenic. Toporescu and Geloso and Levy, according to Kolthoff<sup>(7)</sup> had already observed that, up from a certain level, the increase of the concentration of ammonium hydroxide had but a small effect on the carrying down of copper.

Another resource tried was the double precipitation of ferric hydroxide. After the first precipitation, the hydroxide was dissolved with hydrochloric acid and again precipitated. In these conditions, the behaviour of both copper and arsenic was studied. The results in Table II.4 show that, even after two precipitations of ferric hydroxide, the mass of copper in the precipitate is still eight times that of arsenic. The area of the 0.511 MeV peak of copper-64 remaining in the precipitate is 3.6 times the area of the 0.56 MeV peak of arsenic-76, and in this case the determination of arsenic is not possible, by counting in a sodium iodide scintillation detector.

The case in which copper and arsenic are both present in low concentration was also studied (Tables II.5 and II.6). The simultaneous determination of these two elements is many times required and activation analysis with the help of chemical separation techniques has already been used for this purpose.

Table II.3

Distribution of Copper and Arsenic Between the Liquid Phase and the Precipitate at Higher  $\text{NH}_4\text{OH}$  Concentration

COPPER				ARSENIC	
In the liquid		In the precipitate		In the precipitate	
Percentage	Mass (mg)	Percentage	Mass (mg)	Percentage	Mass ( $\mu\text{g}$ )
99.3	9.9	5.9	0.6	101.7	0.36
98.5	9.8	6.4	0.6	98.3	0.34
99.5	9.9	6.0	0.6	96.1	0.34
97.8	9.8	5.9	0.6	100.4	0.35

Experimental conditions

Mass of copper	= 10 mg	$\text{NH}_4\text{Cl}$ concentration	= 1 M
Mass of arsenic	= 0.35 $\mu\text{g}$	pH	= 9.5
Mass of iron	= 9.6 mg	Final volume	= 14 ml
$\text{NH}_4\text{OH}$ concentration	= 2.5 M		

Table II.4

Carrying of Arsenic and Copper after Double Precipitation of Ferric Hydroxide

ARSENIC		COPPER	
% In the precipitate	Mass in the precipitate ( $\mu\text{g}$ )	% In the precipitate	Mass in the precipitate ( $\mu\text{g}$ )
103.9	9.27	0.7	70
103.8	9.23	0.7	70
102.2	9.12	0.7	70

Experimental conditions

Mass of arsenic	= 8.92 $\mu\text{g}$	$\text{NH}_4\text{Cl}$ concentration	= 1.3 M
Mass of copper	= 10 mg	pH	= 9.3 – 9.7
Mass of iron	= 9.6 mg	Final volume	= 9 ml
$\text{NH}_4\text{OH}$ concentration	= 1.7 – 5 M		

Table II.5

Distribution of Copper Between the Liquid Phase and the  
Precipitate at Low Concentrations

COPPER IN THE LIQUID		COPPER IN THE PRECIPITATE			
%	Mass ( $\mu\text{g}$ )	No Washing		Washing with $\text{NH}_4\text{Cl}$	
		%	Mass ( $\mu\text{g}$ )	%	Mass ( $\mu\text{g}$ )
97.8	24	5.2	1.3	1.8	0.4
100.6	25	5.7	1.4	2.0	0.5
99.6	25	5.2	1.3	1.7	0.4

**Experimental conditions**

Mass of copper = 25  $\mu\text{g}$   
 Mass of arsenic = 35  $\mu\text{g}$   
 Mass of iron = 9.6 mg  
 $\text{NH}_4\text{OH}$  concentration = 2.7 M

$\text{NH}_4\text{Cl}$  concentration = 1 M  
 pH = 9.5  
 Final volume = 11 ml

Table II.6

Distribution of Arsenic Between the Liquid Phase and the  
Precipitate at Low Concentrations

ARSENIC IN THE LIQUID		ARSENIC IN THE PRECIPITATE			
%	Mass ( $\mu\text{g}$ )	No Washing		Washing with $\text{NH}_4\text{Cl}$	
		%	Mass ( $\mu\text{g}$ )	%	Mass ( $\mu\text{g}$ )
0.4	0.1	102.9	36	97.2	34
0.3	0.1	102.7	36	96.9	34
0.2	0.1	104.0	37	99.5	35

Experimental conditions: the same as mentioned in Table II.5

The results of the separation by coprecipitation were very satisfactory and consequently the determination of copper in the supernatant liquid and of arsenic in the precipitate were perfectly feasible.

#### II.4.2 – Analysis of Artificial Samples and of $\text{FeCl}_{3.6}\text{H}_2\text{O}$

The next step was the analysis of an artificial sample containing both activated elements. After the separation of the liquid and solid phases, the washing was added to the supernatant liquid.

The results were satisfactory, as is shown in Table II.7.

Table II.7

Results of the Analysis of Synthetic Samples Containing Copper and Arsenic

SAMPLE	MASS OF COPPER DETERMINED ( $\mu\text{g}$ )	MASS OF ARSENIC DETERMINED ( $\mu\text{g}$ )
1	13.5	9.45
2	12.7	9.60
3	12.7	9.60
4	13.2	9.45
5	13.5	9.30

#### Experimental conditions

Mass of copper added	= 14.0 $\mu\text{g}$	$\text{NH}_4\text{OH}$ concentration	= 4.3 M
Mass of arsenic added	= 9.98 $\mu\text{g}$	$\text{NH}_4\text{Cl}$ concentration	= 1.7 M
Mass of iron	= 9.6 mg	Final volume	= 7.2 ml

A similar experiment was carried out by adding the copper and arsenic samples to human hair, which was dissolved and processed as already described.

The hair was first washed with acetone and water and then dried and weighed. After adding the tracers, dissolution was made by heating with a mixture of  $\text{H}_2\text{SO}_4$  and  $\text{HNO}_3$ . The other reagents necessary for the precipitation were added and the solid and liquid phases were separated by centrifugation. The corresponding data are presented in Table II.8.

A sample of a Carlo Erba p.a. reagent,  $\text{FeCl}_{3.6}\text{H}_2\text{O}$ , was also analyzed. It was irradiated in a plastic container, for eight hours, together with copper and arsenic standards. After the irradiation, the salt was transferred to a centrifuge tube, ammonium chloride was added and the iron precipitated with ammonium hydroxide.

After centrifugation and washing with 1M  $\text{NH}_4\text{Cl}$ , the supernatant liquid and the washings were mixed. Copper in the liquid was precipitated with ammonium sulfide. The filter paper containing the precipitate was transferred to a plastic counting tube and its activity measured in a sodium iodide scintillator. The ferric hydroxide precipitate was dissolved in hydrochloric acid and taken to volume in a 25 ml flask, a 2 ml aliquot being taken for counting. The results of the analysis are in Table II.9.

Table II.8

Determination of Copper and Arsenic Added to a Sample of Human Hair

MASS OF COPPER ( $\mu\text{g}$ )		MASS OF ARSENIC ( $\mu\text{g}$ )	
ADDED	FOUND	ADDED	FOUND
9.81	9.73	8.92	8.26
9.81	9.58	8.92	7.90
9.81	9.31	8.92	8.32

## Experimental conditions

Mass of hair = 24 to 25 mg  
 Mass of iron = 9.6 mg  
 $\text{NH}_4\text{Cl}$  concentration = 1.1 M  
 pH = 9.5  
 Final volume = 34 to 42 ml

Table II.9

Results of the Analysis of the Reagent  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ 

ELEMENT FOUND	
COPPER (ppm)	ARSENIC (ppm)
1.7	3.5

## Experimental conditions

Mass of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  = 151.74 mg  
 $\text{NH}_4\text{Cl}$  concentration = 1.4 M  
 pH = 10  
 Final volume = 43 ml



### II.5 – Separation of Arsenic and Antimony by Coprecipitation of Arsenic with Ferric Hydroxide

The simultaneous determination of arsenic and antimony by non destructive activation analysis using sodium iodide scintillation detectors is more difficult still than that of copper and arsenic, due to the closeness of the main peaks of the radioisotopes arsenic-76 and antimony-122.

During an experiment in trying to determine arsenic in a metallic copper sample which also contained antimony it was verified that, contrary to expectation, the carrying down of antimony by ferric hydroxide was less than that of arsenic. This fact was observed with the aid of a Ge(Li) solid state detector. It was then thought of the possibility of developing a separation method for the two elements by coprecipitation with ferric hydroxide.

In the first experiments the conditions used were similar to the ones employed for the separation of copper and arsenic. The determination of the percentage of antimony carried down was done by the counting of the activity in the precipitate of the radioisotope antimony-122, of 2.68 days half-life. By the data in Table II.10, it can be observed that the carrying of antimony was of about 75%.

Table II.10

Carrying of Antimony by Ferric Hydroxide

SAMPLE	% CARRIED
1	76.9
2	73.8
3	75.4

#### Experimental conditions

Mass of arsenic	= 0.35 $\mu$ g
Mass of antimony	= 0.33 $\mu$ g
Mass of iron	= 9.6 mg
NH <sub>4</sub> OH concentration	= 2.8 M
NH <sub>4</sub> Cl concentration	= 1.5 M
pH	= 9.5
Final volume	= 8 ml

Later it was seen that an increase in pH would favor the permanence of antimony in the liquid phase (Table II.11). Since the presence of ammonium chloride has an effect in lowering the pH, it was tried to eliminate this reagent to work at higher pH.

In these conditions, the washing of the precipitates with 1M NH<sub>4</sub>Cl and 50% NH<sub>4</sub>OH was also tested (Table II.12). Washing with 50% NH<sub>4</sub>OH has practically the same effect as washing with NH<sub>4</sub>Cl, as regards antimony, but it has the disadvantage of eliminating a higher amount of arsenic from the precipitate. On the other hand, it is a well known fact that antimony is complexed by tartaric acid. It was then tried to use this property of antimony to keep a higher fraction of the element in solution.

In Table II.13, the results obtained with and without tartaric acid can be compared. It must be also taken into account that the amount of acid cannot be too high, or else it will prevent the precipitation of ferric hydroxide. The lowest fraction of antimony was carried at a 0.001M concentration in tartaric acid.

Table II.11

Carrying of Antimony as a Function of pH

NH <sub>4</sub> OH MOLARITY	pH	% Sb CARRIED
2.8	9.5	75.4
4.7	9.7	69.5
7.5	9.9	64.6

## Experimental conditions

The same as mentioned in Table II.10

Table II.12

Carrying of Antimony and Arsenic by Ferric Hydroxide in the  
Absence of Ammonium Chloride

SAMPLE	% ANTIMONY CARRIED			% ARSENIC CARRIED		
	NO WASHING	WASHING	WASHING	NO WASHING	WASHING	WASHING
		WITH 1M NH <sub>4</sub> Cl	WITH 50% NH <sub>4</sub> OH		WITH 1M NH <sub>4</sub> Cl	WITH 50% NH <sub>4</sub> OH
1	50.9	—	—	107.5	—	—
2	54.6	—	—	103.3	—	—
3	53.4	—	—	104.9	—	—
4	56.5	50.8	45.3	102.4	101.4	93.7
5	54.3	49.4	45.2	102.8	102.2	96.1
6	55.6	51.2	46.1	103.5	102.9	99.4

## Experimental conditions

Mass of arsenic = 35  $\mu$ g  
 Mass of antimony = 33  $\mu$ g  
 Mass of iron = 9.6 mg

NH<sub>4</sub>OH concentration = 4 M  
 pH = 11.2  
 Final volume = 7.5 – 8 ml

Table II.13

Influence of Tartaric Acid on the Carrying of Antimony

SAMPLE	% OF ANTIMONY CARRIED			
	NO ACID	WITH 0.0005 M ACID	WITH 0.0010 M ACID	WITH 0.0015 M ACID
1	69.8	37.3	25.5	23.8
2	63.5	36.8	24.1	23.3
3	62.5	35.4	24.1	23.5

**Experimental conditions**

Mass of antimony	= 8.25 $\mu\text{g}$	$\text{NH}_4\text{OH}$ concentration	= 5 M
Mass of arsenic	= 49.6 $\mu\text{g}$	pH	= 11
Mass of iron	= 9.6 mg	Final volume	= 14 ml

The influence of the pH was also studied with the use of tartaric acid. The results in Table II.14 show that the pH range which most favours the remaining of antimony in the supernatant liquid is the one between 10.6 and 11.0.

Table II.14

Influence of pH on the Carrying of Antimony, in the Presence of Tartaric Acid

pH	% ANTIMONY CARRIED
9.3	38.2
10.0	30.4
10.2	24.2
10.6	21.5
10.8	22.8
11.0	20.8

**Experimental conditions**

Mass of antimony	= 82.5 $\mu\text{g}$	Tartaric acid concentration	= 0.001 M
Mass of arsenic	= 49.8 $\mu\text{g}$	Final volume	= 14 ml
Mass of iron	= 9.6 mg		

Once these conditions were established, a series of experiments to test the reproducibility of the results were done (Table II.15). The experimental conditions, in terms of mass of antimony, varied somewhat, but always in the low concentration range.

**Table II.15**  
Study of the Reproducibility of the Experimental  
Results of Antimony Carrying

SAMPLE	% OF ANTIMONY IN THE PRECIPITATE
1	23.8
2	23.3
3	23.5
4	25.5
5	24.1
6	27.9
7	20.2
8	20.7
9	23.2
10	24.2
11	31.1
12	22.8
13	21.0
14	20.6
15	24.6
16	24.7
17	24.4
18	24.2
19	24.1
20	23.9

**Experimental conditions**

Mass of antimony	= 0.001 M	NH <sub>4</sub> OH concentration	= 5 to 7.5 M
Mass of iron	= 9.6 mg	Tartaric acid concentration	= 0.001 M
pH	= 11		

At the same time, the behaviour of arsenic V was studied, in the conditions chosen to minimize the coprecipitation of antimony (Table II.16)

**Table II.16**

Carrying of Arsenic V by Ferric Hydroxide in the Presence of Tartaric Acid

SAMPLE	% OF ARSENIC IN THE PRECIPITATE
1	89,3
2	89,2
3	86,8
4	87,2
5	85,6
6	88,0

**Experimental conditions**

Mass of arsenic	= 2.36 $\mu\text{g}$	pH	= 11
Mass of antimony	= 1.65 $\mu\text{g}$	Final volume	= 13 ml
Mass of iron	= 9.6 mg	Tartaric acid concentration	= 0.001 M
$\text{NH}_4\text{OH}$ concentration	= 5.5 M		

In an attempt to still improve the separation of the two elements, experiments were done with reprecipitation of ferric hydroxide (Table II.17). The precipitate was dissolved with concentrated nitric acid and reprecipitated with ammonium hydroxide. The pH was adjusted to the desired value. The precipitates were counted in the centrifuge tube itself.

**Table II.17**

Carrying of Arsenic and Antimony After the Double Precipitation of Ferric Hydroxide

ARSENIC IN THE PRECIPITATE		ANTIMONY IN THE PRECIPITATE	
%	MASS ( $\mu\text{g}$ )	%	MASS ( $\mu\text{g}$ )
88,5	2,1	11,4	0,19
88,4	2,1	10,3	0,17
86,4	2,0	12,4	0,20
86,3	2,0	11,0	0,18
87,4	2,1	12,4	0,20
88,8	2,1	—	—

**Experimental conditions**

The same as mentioned in Table II.16

### III – DISCUSSION AND CONCLUSIONS

#### III.1 – Separation of Copper and Arsenic

In the case where the mass of copper (10 mg) is much bigger than that of antimony (0.35  $\mu\text{g}$ ) even if the separation attained is very good, it is still not possible to determine arsenic in the precipitate. After two precipitations of ferric hydroxide and with a mass ratio of 1100 between copper and arsenic the problem was still not solved and the area of the 0.511 MeV peak of  $^{64}\text{Cu}$  was 3.6 times higher than the area of the 0.56 MeV peak of  $^{76}\text{As}$ .

When the masses of the two elements are of the same order (Tables II.5 and II.6), both of them being present in low concentration, the results obtained are good, with one precipitation only. In the supernatant liquid the mass of copper, after the separation, is 240 to 250 times greater than that of arsenic and in the precipitate the contrary occurs, i.e., the mass of antimony is 68 to 87 times the mass of copper. In these conditions, the determination of both elements by counting in a NaI(Tl) scintillation detector is possible.

As for the analysis of artificial samples containing copper and arsenic, the relative standard deviations and relative errors were calculated, as can be seen in Table III.1. The precision and accuracy of the method can be considered good from these data as regards the analysis of microquantities.

Table III.1

Precision and Accuracy in the Analysis of Artificial Samples  
Containing Copper and Arsenic

SAMPLE	ELEMENT ANALYZED	$\mu\text{g}$ ADDED	AVERAGE $\mu\text{g}$ FOUND	STANDARD DEVIATION	RELATIVE STANDARD DEVIATION (%)	RELATIVE ERROR (%)
COPPER (1) +	COPPER	14.0	13.2	0.4	3.0	5.7
ARSENIC	ARSENIC	10.0	9.5	0.1	1.0	5.0
COPPER (2) +	COPPER	9.8	9.5	0.2	2.1	2.7
+ ARSENIC	ARSENIC	8.9	8.2	0.2	2.4	8.5
+ HUMAN HAIR						

(1) Table II.7

(2) Table II.8

The masses determined in the analysis were, for both arsenic and copper, lower than the masses added. This fact can be attributed to losses during the process of analysis, since no carriers were added in the initial separation steps.

The total error was calculated by the equation of Mc Farren et al.<sup>(8)</sup>

$$\text{Total error} = \frac{d + 2s}{\mu} \times 100 \quad (III.1)$$

$d$  = absolute value of the mean error

$s$  = standard deviation

$\mu$  = real value

The analytical methods are so divided in three categories.

- a. Excellent — total error of 25% or less
- b. Acceptable — total error of 50% or less
- c. Unacceptable — total error of more than 50%.

Eckschlager<sup>(3)</sup>, on the other side, remarks that Mc Farren does not take into account the statistical meaning of the mean error. He suggests then a similar expression:

$$\text{Total error} = \frac{d + 2s}{\mu} \times 100$$

Where  $d$  is the absolute value of the mean error, which is statistically significantly different from zero. When the mean error is not significantly different from zero, we have:

$$\text{Total error} = \frac{2s}{\mu} \times 100 \quad (III.2)$$

The statistical significance of the difference of  $d$  from zero can be tested by means of Student's  $t$ -test, at a significance level  $\alpha = 0.05$  and  $\gamma = n-1$  degrees of freedom, where  $n$  is the number of experiments done.

If we now apply equation III.1 to the data obtained in the analysis of the artificial sample containing copper and arsenic we will obtain a value for the total error of 11.4% in the case of copper and of 7.0% in the case of arsenic. The method can then be considered as excellent, according to Mc Farren's criterion.

As to the analysis of the sample of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (Carlo Erba), the presence of copper and arsenic was confirmed through the determination of the half-lives of the corresponding radioisotopes. For  $^{64}\text{Cu}$ , the half-life obtained was of 11.8 hours and for arsenic 26.0 hours. In the case of the standards used, the values determined were 12.6 hours and 26.5 hours, respectively. The tabulated values being 12.8 and 26.4 hours, we can consider that a reasonable agreement was obtained.

Of the elements listed as impurities of the reagent  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (zinc, alkalines and alkaline-earths) none of them is expected to cause any serious interference in the region of the peaks of copper and arsenic, due to the nuclear characteristics of the respective nuclides.

In the spectrum of the ferric hydroxide precipitate (Figure 3.1) the peaks of 1.10 and 1.29 MeV of  $^{59}\text{Fe}$  appear but they do not interfere with the 0.56 MeV peak of  $^{76}\text{As}$ .

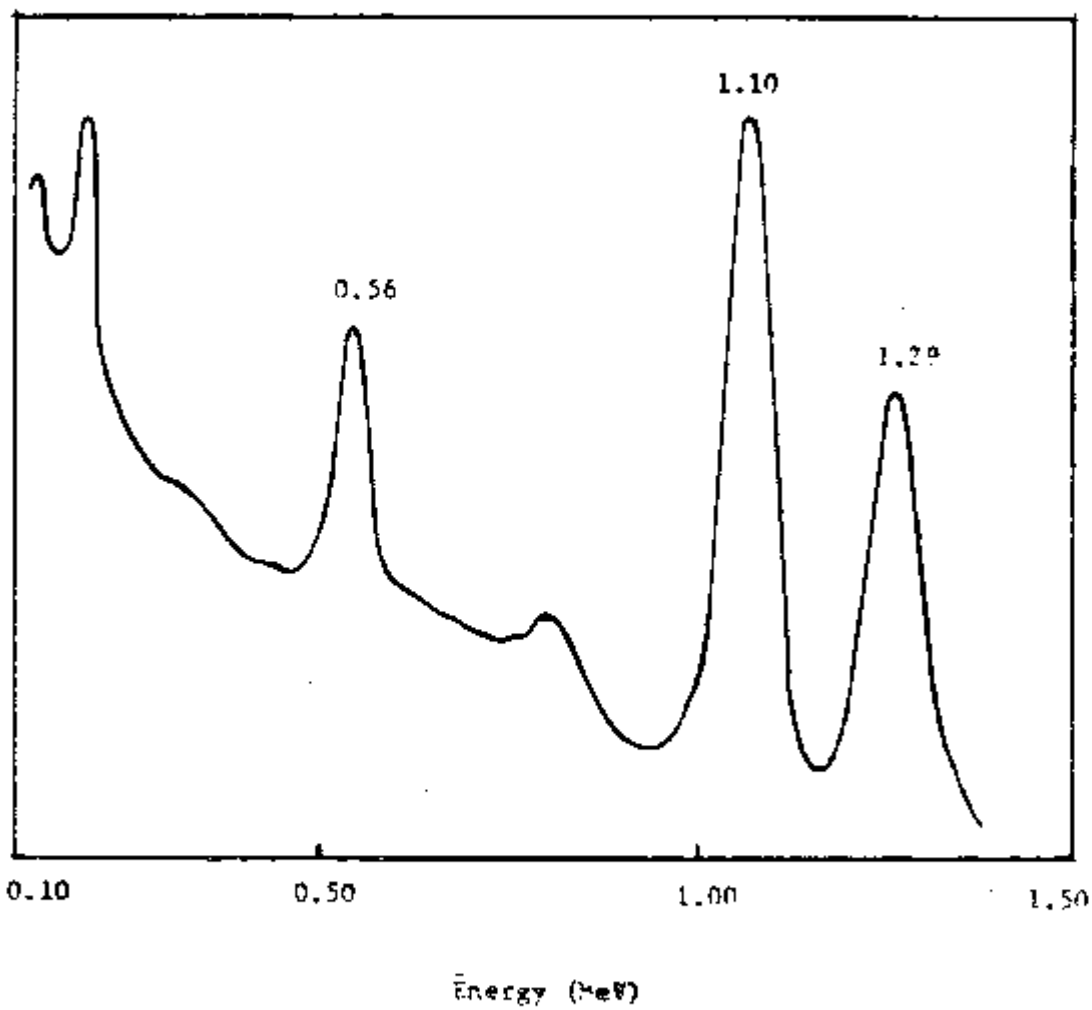


Figure 3.1 - Spectrum of the Ferric Hydroxide Precipitate



In the spectrum of the copper sulfide precipitate (Figure 3.2), besides the 0.511 MeV peak of copper 64, only the peaks of  $^{59}\text{Fe}$  were identified. The energies of 0.41 and 0.82 MeV could not be unequivocally identified, because the poor counting statistics prevented the exact determination of the corresponding half-lives.

It must be remarked that the application of the coprecipitation of ferric hydroxide as a separation method for the determination of copper and arsenic by activation analysis will be limited by the presence of interfering elements, because the carrying by the precipitate is not specific for arsenic.

As regards the experiments with arsenic and antimony, it can be seen by the results in Table II.17 that it was possible to obtain an appreciable enrichment of arsenic in the precipitate and of antimony in the supernatant liquid, when two precipitations were done. The carrying of arsenic by ferric hydroxide was not so complete in this case, probably due to the presence of tartaric acid.

The possibility of determining the two elements with a reasonable accuracy after the separation will depend on their mass ratio and also on the decay time. In the case of the results of Table II.17, in which the final mass of arsenic in the precipitate is approximately 13 times that of antimony and taking into consideration that arsenic is more activated than antimony, the analysis of the first element will be favored just after irradiation. After a decay time of 24 hours, the activity corresponding to the area of the peak of antimony would be of about 5% that of arsenic in the precipitate. As for the determination of antimony in the liquid phase the contrary would occur, due to the more rapid decay of arsenic. After 24 hours, the activity of arsenic in the liquid phase would be of about 30% of the antimony activity, which would hinder the determination of this element. After 137 hours of decay, the activity of arsenic would be less than 4% that of antimony.

The carrying by colloidal precipitates such as ferric hydroxide of species present in solution is generally attributed to surface adsorption or occlusion phenomena. Egorov<sup>14)</sup> mentions the possibility of formation of compounds, like manganites, titanates, aluminates or ferrites. In the specific case of the coprecipitation of copper as the ammoniacal complex, Kolthoff and Moskovitz<sup>17)</sup> showed that aging at room temperature or at 98°C promotes a slow incorporation of copper to the precipitate. Furthermore, on heating, the amount of coprecipitated copper grows up, which is contrary to the coprecipitation rules. This fact is attributed by the authors to the slow formation of a copper ferrite.

Kolthoff and Moskovitz<sup>17)</sup> share the opinion that the increase in the ammonium hydroxide concentration implies in a greater stability of the ammoniacal complex and, as a consequence, in a decrease in the coprecipitation. The presence of the  $\text{NH}_4^+$  ions, on the other hand, lowers the concentration of  $\text{OH}^-$ , which also decreases the carrying of copper.

No references were found in the literature about the mechanism of coprecipitation of arsenic and antimony with ferric hydroxide. Arsenic forms with iron a basic salt, iron arsenite, of variable composition, which indicates the possibility of carrying by chemical compound formation.

Last but not least we should emphasize the possibilities of using the phenomenon of coprecipitation, with ferric hydroxide or with other precipitates, as a method of separation. A change in pH, which is the method utilized by Russian researchers or other means like oxidation or complexation of species can be used to keep some of them in solution and to promote the carrying of others.

In this way, a method initially used for the elimination of unwanted impurities or for the concentration of elements present at trace levels can be also used as a valuable separation process, for works at low concentrations.

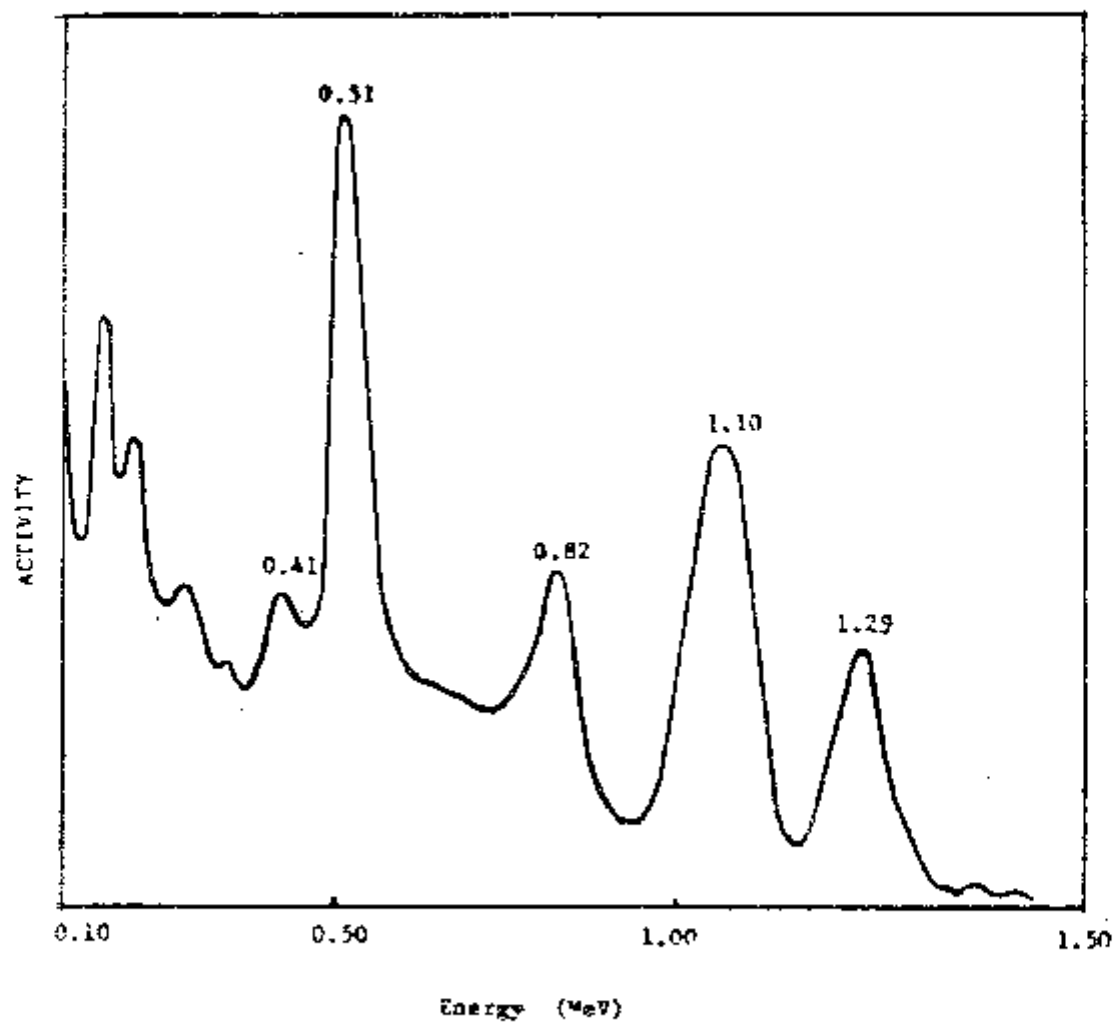


Figure 3.2 - Spectrum of the Copper Sulfide Precipitate

## RESUMO

No presente trabalho, estuda-se um método de separação química para os pares cobre-arsênio e arsênio-antimônio, por coprecipitação com hidróxido férrico. A determinação destes pares de elementos é um tanto difícil por análise por ativação, devido aos valores muito próximos das energias dos raios gama emitidos pelos respectivos radioisótopos formados por ativação com nêutrons térmicos. Estuda-se a eficiência da separação e o processo é aplicado à análise, por ativação, de amostras artificiais contendo cobre e arsênio e de um reagente p.a.,  $\text{FeCl}_3 \cdot \text{H}_2\text{O}$ . Quanto ao par arsênio-antimônio, somente a separação é estudada, determinando-se a distribuição dos dois elementos entre as fases líquida e sólida.

O cobre é mantido em solução por complexação com hidróxido de amônio e o antimônio por complexação com ácido tartárico.

A distribuição dos elementos entre as fases líquida e sólida é acompanhada por contagem das atividades dos radioisótopos cobre-64, arsênio-76 e antimônio-122.

Finalmente, dá-se ênfase às possibilidades que apresenta o método de separação por coprecipitação para trabalhos em baixas concentrações.

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