



**STUDY OF THE INFLUENCE OF VARIOUS FACTORS ON  
THE RADIOCHEMICAL — GUTZEIT METHOD OF  
ACTIVATION ANALYSIS OF ARSENIC**

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STUDY OF THE INFLUENCE OF VARIOUS FACTORS ON THE RADIOCHEMICAL-  
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SUMMARY

Study of various factors that might influence recovery of arsenic in the radiochemical-Gutzeit method of analysis of arsenic was done. The factors examined were method of digestion of samples, time of reaction, amount of iron ions, amount of stannous ions, interference caused by the presence of antimony and copper, effect of agitation of reaction flasks on abbreviating the time of reaction and amount of arsenic carrier required for a high recovery of arsenic. Precision and accuracy of the proposed method were determined.

INTRODUCTION

Quantitative analysis of small amounts of arsenic in various materials is frequently made by the Gutzeit technique or its modifications<sup>(1)</sup>.

The method is based on the formation and evolution of arsine and interaction of the liberated arsine with a mercuric salt deposited on filter paper strips. A yellow-brown compound is formed on the paper strip and the length and intensity of the color is compared with the color formed when known amounts of arsenic is analyzed by the same method<sup>(1)</sup>. The method is used for amounts from one to 500 micrograms of arsenic.

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Visual comparison of color intensity is always influenced by a subjective factor and precision and accuracy are, consequently, rather poor.

However, the merits of the classical method in connection with simplicity and sensitivity are high and association of that technique with radioanalytical ones increases its usefulness, specially regarding higher sensitivity. The Radiochemical-Gutzeit method is highly appropriate when a large number of samples have to be contemporaneously analyzed, specially taking into account that the original simplicity of the method can be maintained when using radiochemical techniques.

Such a situation of analysis of a large number of samples occurred when of the study of "in vitro" distribution of arsenic along single hairs, Lima<sup>(2)</sup> and Atalla, Silva and Lima<sup>(3)</sup>. Very long hairs, of about 30 to 40 centimeters length, cut in fractions of one centimeter, had to be analyzed for arsenic in the range of tenths of parts per million and larger. The total number of samples amounted to 30 per set of analysis.

Use of the Gutzeit technique associated with activation analysis, for the determination of arsenic, had already been made by Smith<sup>(4)</sup> and by Foldzinska and Malinowski<sup>(5)</sup>. In the work of Smith<sup>(4)</sup> the following analysis steps were investigated: dissolution of sample, evolution time of arsine, form of zinc and reaction mixture temperature. Evolved arsine was collected in a trap containing mercuric chloride solution. The apparatus for formation and evolution of arsine was not described but the method, in accordance with Smith<sup>(4)</sup>, is a modification of Thomas and Collier's Gutzeit technique<sup>(6)</sup> who used a relatively large and complex equipment.

In the work of Foldzinska and Malinowski<sup>(5)</sup> a very simple equipment is used in which the arsine is made to react with the mercuric salt deposited on filter paper. However, no system-

atic examination was made in connection with the various factors that might influence the recovery of arsine, such as reaction time, temperature, agitation of the reaction flasks, interference of other elements, etc.

In order to use the radiochemical-Gutzeit method and in this way to expedite the analytical process for the hair samples, the following steps were studied in the present work: method of digestion of samples, amount of arsenic carrier, interference caused by antimony and by copper, influence of amount of iron ions to inhibit evolution of stibine, influence of agitation of reaction vessels on the time of formation and evolution of arsine and, finally, determination of the precision and accuracy of the method.

#### DISGESTION METHOD

The recovery of arsenic in organic material when of the destruction of organic matter has been studied by Gorsuch<sup>(7)</sup>. In Gorsuch's work recovery of practically 100 per cent was achieved by using wet digestion with the following mixtures: nitric and perchloric acids, nitric-perchloric-sulfuric acids, nitric-sulfuric acids.

Nitric-sulfuric acids mixture was tried for hair and filter paper samples using the same 125 milliliters erlenmeyers flasks in which the arsine formation reaction was to take place later, (see Figure I). Recovery was of the order of 70 per cent, probably due to the short neck reaction flask. Results are presented in Table I.

Other oxidating agents and mixtures such as hydrogen peroxide-sulfuric acid, potassium chlorate and potassium permanganate, were also tried with no better results than the mixture nitric-sulfuric acid.

Digestion with sulfuric acid only gave better results,

as indicated in Table II, and this procedure was used throughout the rest of the experiments.

T A B L E I

Recovery of arsenic using nitric-sulfuric acids as digestion mixtures

Material	Mass mg	<sup>76</sup> As added cpm	<sup>76</sup> As recovered cpm	Recovery %
Hair	103	13103	8476	65
Filter Paper	50	13103	9221	70
Filter Paper	12	11608	7938	68

T A B L E II

Recovery of arsenic using sulfuric acid for digestion of samples

Material	Mass mg	<sup>76</sup> As added cpm	<sup>76</sup> As recovered cpm	Recovery %
Hair	3	5838	5877	100.7
"	27	5619	5582	99.3
"	180	5803	5206	100.0
"	265	5622	5582	99.3
Paper	50	3934	3741	95.1
"	50	3934	3850	98.0

AMOUNT OF ARSENIC TO BE USED AS CARRIER

Since the circular filter paper imbibed in the mercuric chloride solution has a limited surface to interact with the arsine, it is necessary that the amount of arsenic present in the reaction flask does not exceed a certain maximum. This means that

the amount of arsenic carrier to be added to the irradiated sample must not be too large.

In order to check the maximum amount of arsenic carrier that may be used, a labelled solution of  $^{76}\text{As}$  (as sodium arsenite) was prepared and ten aliquots of this solution, containing one microgram each of labelled arsenic, were taken. To each of these aliquots inactive arsenic (sodium arsenite) was added in order to make solutions with a total arsenic content of 10, 20, 30 ... 100 micrograms of arsenic. The solutions were processed as described in the method (see Method). The amount of arsenic trapped in the mercuric chloride paper was determined by counting the papers and comparing with the corresponding counting for the arsenic initially present in each reaction flask.

It was verified that the recovery of arsenic was practically total in all flasks, indicating that an amount of arsenic carrier up to 100 micrograms could be used. However, above 40 micrograms of arsenic carrier, the yellow-brown spot formed on the mercuric paper was slightly irregular and this might introduce errors when counting the samples in beta counters. For this reason an amount of 30 micrograms as arsenic carrier was chosen and used in all subsequent experiments.

#### INTERFERENCE OF ANTIMONY AND COPPER

In the classical Gutzeit method antimony, when present in amounts above 100 micrograms, interferes with the determination of arsenic since it may evolve as stibine and reacts with the mercuric salt forming a compound whose color masks the one formed by arsine.

Activation analysis associated with the Gutzeit separation technique will not prevent, in a direct manner, this interference since the characteristics of the radiation emitted by



$^{122}\text{Sb}$  are quite similar to the one emitted by  $^{76}\text{As}$ .

Copper, which is an element frequently found in hair, may also interfere if counting is carried out with NaI(Tl) gamma counters since resolution of these counters is not sufficient to resolve the annihilation peak at 0.51 MeV of  $^{64}\text{Cu}$  and the peak at 0.55 MeV of  $^{76}\text{As}$ . Table III gives the nuclear data of importance for activation analysis, with thermal neutrons, of arsenic, antimony and copper.

TABLE III

Nuclear data for arsenic, antimony and copper

Natural Isotope	Abundance	Cross section (barns)	Isotope formed	$t_{1/2}$ (hours)	Energy of radiation (MeV)	
					beta	gamma
$^{75}\text{As}$	100	4.3	$^{76}\text{As}$	26.7	2.96-2.41	0.55-1.19
$^{121}\text{Sb}$	57	7	$^{122}\text{Sb}$	67.2	1.4-1.98	0.56-1.2
$^{63}\text{Cu}$	69	4.4	$^{64}\text{Cu}$	12.8	0.57	0.34-0.51

In order to study the interference of antimony, small amounts of an antimony chloride solution were placed in filter paper discs which were dried and irradiated with thermal neutrons. After irradiation, the activity in the papers were determined, the papers were placed in the processing apparatus, Figure 1, and inactive antimony chloride solution, in different amounts, added in each flask. Inactive arsenic solution (30  $\mu\text{g}$  of arsenic) was added and the filter paper samples were processed as if for the analysis of arsenic (see Method). Table IV gives the results concerning the amount of antimony that evolved and was trapped in the mercuric chloride filter paper discs.

T A B L E IV

Interference of antimony on arsenic determination

Mass of Sb ( $\mu\text{g}$ )	Activity added ( $^{122}\text{Sb}$ ) (cpm)	Activity on mercuric paper (cpm)	Percentage of $^{122}\text{Sb}$ evolved
50	5344	129	2.4
100	5605	126	2.2
200	6150	144	2.3
400	6060	137	2.2
500	5674	112	1.9
800	5900	94	1.6
1000	5636	25	0.4
1500	5500	126	2.3

The same technique was used to check interference of copper. In this case no activity was found, above background, on the mercuric paper.

The percentage of antimony that evolves as stibine is slightly larger when its amount is small; this percentages gradually decreases when the total amount of antimony increases up to about one milligram of antimony and starts growing again. For one milligram the percentage of antimony evolved is of the same order of magnitude of the statistical counting error. This amount of hold-back antimony carrier was subsequently used for all experiments.

INFLUENCE OF AMOUNT OF IRON IN SOLUTION

In the classical method of Gutzeit, iron is used to prevent stibine formation without interfering with formation and evolution of arsine. The amount of 350 milligrams of ferric ions is recommended by Scott<sup>(1)</sup> for a total volume, of the arsenic solution, of 50 milliliters. Since the use of radioisotope techniques

allows a much higher sensitivity for checking such a type of interferences, it was decided to study the influence of growing amounts of iron ions in the evolution of arsine, and on the retention of antimony. One set of filter papers were impregnated with antimony chloride and another set with sodium arsenite. The papers were irradiated, let to cool for about 20 hours in order that the activity due to  $^{38}\text{Cl}$  (37.3 minutes half-life) would disappear, the activities were determined and then they were separately processed as for arsenic analysis (see Method), adding the inactive amounts of carriers of antimony and arsenic, as prescribed in the Method. Amounts of arsenic and antimony evolved and caught in the mercuric trap of impregnated filter paper were determined. Table V presents the results.

TABLE V

Influence of iron ions on the evolution of arsine and retention of antimony

Fe Cl <sub>3</sub> (mg Fe)	Activity of $^{76}\text{As}$ (cpm)			Activity of $^{122}\text{Sb}$ (cpm)		
	Initial	Recovered (Hg paper)	%	Initial	Recovered (Hg paper)	%
0	10 050	10 395	99	8 040	1 206	15
17	9 214	9 306	101	8 250	990	12
35	9 500	9 215	97	7 900	1 027	13
70	10 206	10 002	98	8 450	250	3
105	8 992	8 722	97	7 731	230	3
140	9 640	9 640	100	8 560	340	4
175	10 156	10 359	102	8 640	170	2
280	10 200	8 262	81	8 133	160	2
560	10 360	8 081	78	8 242	82	1

Table V shows that the inhibition of stibine formation is proportional to the amount or concentration of iron ions. However when this amount is above 175 milligrams of iron ions, arsine

formation is also restrained. For this reason the amount of 100 milligrams of ferric ions was adopted.

#### INFLUENCE OF AMOUNT OF STANNOUS IONS

In accordance with Scott<sup>(1)</sup> stannous chloride is essential to the complete evolution of arsine.

The total amount of arsenic to be evolved as arsine, by associating the Gutzeit technique with activation analysis, is of the order of 30 to 40 micrograms in arsenic (carrier plus arsenic to be analyzed). For this amount of arsenic, variation of the amount of stannous ions from 400 to 1600 milligrams was not critical giving a recovery of arsenic, in the mercuric filter paper, of practically 100 per cent. The amount of 400 milligrams of stannous chloride was then adopted as it will be described in the Method.

#### INFLUENCE OF AGITATION OF REACTION FLASKS ON TIME OF REACTION

In order to check the time for complete evolution of arsine when the reaction flasks are agitated throughout the reaction process, the flasks were placed over a vibratory plate that would vibrate with a frequency of 170 movements per minute and an amplitude of half a centimeter. For comparison an equal number of reaction flasks were used without agitation. For the flasks on agitation the reaction was left to take place for half an hour and one hour; in the standing flasks the reaction took place for three hours, which was a time that previous experiments had shown the reaction to be complete after that time. In each flask about one milligram of an alloy of Fe-As (iron metal wire used for standardization) was processed. The alloy had been irradiated for eight hours at  $5 \times 10^{12}$  n/s.cm<sup>2</sup>. Table VI gives the results.

TABLE VI

Influence of agitation on time of reaction

	Agitating reaction flasks		Standing reaction flasks
	0.5 hour	1.0 hour	3.0 hours
	23.244*	23.940	24.001
	21.356	25.314	23.359
	24.169	24.113	24.709
	22.496	23.921	24.669
Mean:	22.816	24.322	24.185
Standard deviation of a single result:	1.19	0.67	0.64

\* Units: area under the peak of 0.55 MeV, per milligram of iron.

An analysis of variance (F test)<sup>(8), (9)</sup> carried out with the results of Table VI, considering three treatments and four repetitions with  $2n-2=2 \times 4-2=6$  degree of freedom, gives a F value of 3.66 which is not significant at the 5% level. This indicates that by agitating the flasks the reaction time can be abbreviated to one or even half an hour. With half an hour the spreading of the data is a bit larger than with an hour as indicated by a larger standard deviation for half an hour reaction. In the method to be described (see Method) the one hour reaction time was used.

#### METHOD

Based on the described experiments in connection with digestion of sample, amount of arsenic to be used as carrier, interference of antimony and copper, influence of amount of iron ions, influence of amount of stannous ions and influence of

agitation of reaction flasks, at room temperature, the following Gutzeit radiochemical method for analysis of arsenic was developed.

### Reagents

**Arsenic carrier solution:** 30  $\mu\text{g}$  As/ml. Dissolve arsenious oxide with drops of sodium hydroxide 40 % and make up to volume, with water, in a volumetric flask.

**Antimony carrier solution:** 10 mg Sb/ml. Dissolve antimony chloride in concentrate hydrochloric acid and make up to volume with same strength acid.

**Ferric solution:** 100 mg Fe/ml. Dissolve ferric chloride in water and dilute to obtain the required concentration.

**Stannous solution:** 400 mg  $\text{SnCl}_2$ /ml. Dissolve stannous chloride in hydrochloric acid 1:1 and make up to volume with same strength acid.

**Filter paper imbibed in a 5% alcoholic solution of mercuric chloride.** Let to dry at room temperature and use paper recently prepared.

**Cotton wool imbibed in a 10% solution of lead acetate to which some drops of acetic acid was added.** Squeeze excess solution and let to dry. Use a recently prepared cotton wool as described.

**Sodium iodide solution:** 150 mg NaI/ml. Dissolve sodium iodide in water and dilute to obtain the required concentration.

### Method

Samples containing from hundredths of micrograms up to ten micrograms of arsenic are placed into polyethylene bags and irradiated for about 8 hours in a flux of  $5 \times 10^{12}$  n/s.cm<sup>2</sup>. One to two milligrams of arsenious oxide is prepared and irradiated in the same way and used as standard.

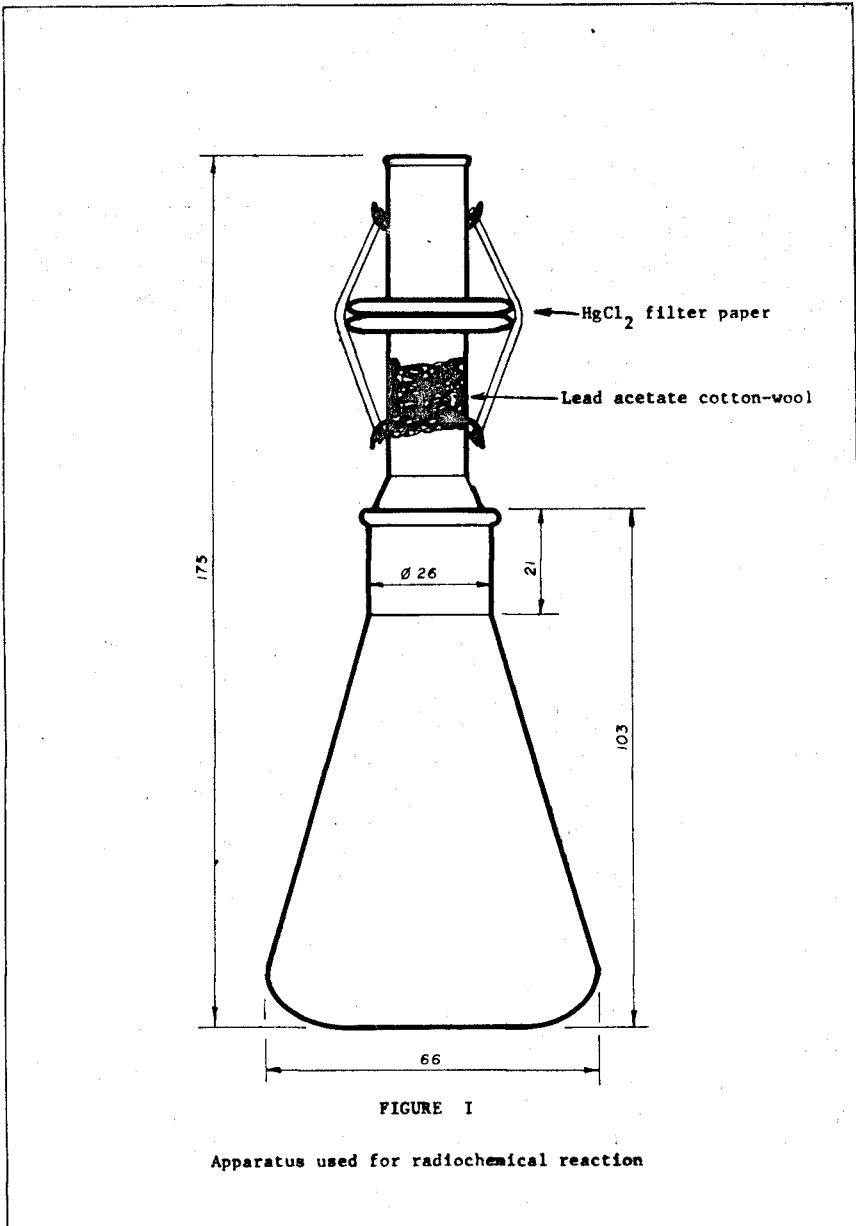
After irradiation the arsenious oxide is dissolved with drops of sodium hydroxide solution at 40% and made up to 100 milliliters. Two milliliters of this are taken and again made up to 100 milliliters; one milliliter of this last solution is transferred to a counting vial and used as standard.

The irradiated samples are removed from the polyethylene bags and transferred to the processing flasks (Fig. I). One milliliter of the arsenic carrier solution is added and the sample is digested, with gentle heating, with 6 milliliters of concentrate sulfuric acid for about half an hour. The flask is let to cool and 90 milliliters of water are carefully added. One tenth of a milliliter of the antimony carrier solution, one milliliter of the ferric chloride solution, one milliliter of the stannous chloride solution and five milliliters of sodium iodide solution\* are added, and the flask let to stand for about 15 minutes. Ten grams of zinc pellets (pieces of about five millimeters size) are added and the top part of the apparatus, with the mercuric chloride filter paper and lead acetate cotton wool to retain any hydrogen sulfide evolved from the mixture, is immediately adapted. The ground glass joint is previously lubricated with water. The flasks are placed over the vibrating board and the reaction is let to proceed for about one hour when the filter papers are removed and mounted for counting.

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\* Sodium iodide is used as hold-back carrier for sodium when analysing biological materials.

If counting is to be made with Geiger counters for solid samples the filter paper discs are mounted in the usual way. If NaI(Tl) crystals of the well type are used for counting, the papers are transferred to counting vials. The activities are compared with that of the arsenic standard which is counted in the same way and mounting as the samples.





### Precision and Accuracy of the Method

In order to check precision of the proposed method, ten samples of an iron-arsenic alloy were analyzed. Samples of about one milligram of iron alloy and of arsenous oxide to be used as standard were irradiated in a thermal neutron flux of  $5 \times 10^{12}$  n/s.cm<sup>2</sup> for eight hours, let to cool for sixteen hours and processed as described in the Method. Dissolution of iron samples was carried out with one milliliter of concentrate nitric acid to which one drop of 1:1 hydrochloric acid had been added. After the sample had been dissolved 6 milliliters of concentrate sulfuric acid were added and the solution was heated until the production of white fumes. From there on the process was followed as described in the method. Counting was carried out in a 400 channels analyser ..... (TMC-404-6) coupled to a 3 x 3 inches NaI(Tl) well crystal. Results are presented in Table VII.

T A B L E VII

Precision of determination of arsenic in high purity iron

Sample	µg As/mg Fe
1	0.2507
2	0.2485
3	0.2519
4	0.2507
5	0.2512
6	0.2428
7	0.2552
8	0.2497
9	0.2534
10	0.2473

Mean:  $\bar{x} = 0.250$

Standard deviation of a single result:  $s_x = 0.003$

Standard deviation of mean:  $s_m = 0.001$

Determination of confidence limits for the results presented at Table VII, at 5% level, gives, from Fisher and Yates Tables<sup>(10)</sup>.

$$P = 0.05$$

$$N = n - 1 = 9$$

$$t = 2.262$$

Hence, every single result has a 95% probability of having the value  $0.250 \pm 0.007$ ,  $(\bar{x} \pm s_x t)$ ; and the average,  $0.250 \pm 0.002$ ,  $(\bar{x} \pm s_m t)$ . On a percent basis these st values are 2.8% and 0.8%, respectively.

Determination of accuracy of the method was made by preparing a sodium arsenite solution labelled with <sup>76</sup>As and dipping into it strands of human hair for about one hour. The hair was removed, washed in running water and dried. Fifteen samples of about 250 micrograms each (about 5 centimeters of a single hair) were separated and let to cool until their activity could be measured with good counting statistics. After determining the activities of the original samples they were processed as described in the Method. Table VIII gives the results.

## DISCUSSION

One of the main disadvantages of the classical Gutzeit method is that all reagents must be "arsenic free". Therefore blanks must be run on all reagents used. The association of the classical Gutzeit technique, in itself a method of very good sensitivity, with activation analysis, would enhance sensitivity and avoid necessity of blank analysis for reagents.

In the classical Gutzeit method many chemical elements such a mercury, platinum, nickel, cobalt and others will interfere with the arsenic determination. By using the radiochemical Gutzeit technique this interference can be eliminated or drastically

T A B L E VIII

Accuracy of determination of arsenic in hair samples

Sample activity*		Recovering (%)
Before processing	After processing	
47 821	46 728	98
43 030	41 619	97
61 721	59 040	96
57 932	57 332	99
50 641	51 309	101
50 312	51 641	103
50 603	50 721	100
42 404	42 737	101
60 700	58 230	96
51 532	51 509	100
20 002	19 614	98
15 181	14 970	99
15 441	15 712	102
17 312	16 874	97
14 931	14 295	96

Mean: 98.9%

\*Units: area under peak of 0.55 MeV.

reduced even when the interfering element is entrained with the evolved arsine and trapped in the mercuric chloride paper, provided the energy of their gamma rays can be resolved when counting with scintillation detectors.

In the case of analysis of arsenic in hair, with very small sample masses, of the order of 50 micrograms or less, the apparatus for the complete analysis, including digestion of samples, is extremely simple. This makes possible the analysis of a very large number of samples at same time.

Sensitivity of the radiochemical-Gutzeit method is much higher than the classical Gutzeit technique. Amounts of 0.0002

micrograms of arsenic, or less, can be determined using neutron fluxes of about  $10^{12}$  n/s.cm<sup>2</sup> and irradiation periods of about 10 hours.

In connection with reproducibility or precision it was seen that, based on a replicate analysis of 10 samples of the same material, single results agree within 2.8% at the 95% probability level and that determination of means has a 95% chance of being within 0.8%. These values are of the same order of magnitude as statistical counting errors.

Accuracy was determined by analysing fifteen samples of known content in arsenic; the average recovering for those 15 analysis was 98.9% with two extreme single values of 96% and one 103%.

In the classical Gutzeit method interference caused by antimony is very serious since even a very small amount of antimony that evolves as stibine will react with the mercuric salt giving higher values for the arsenic determination. The radio-chemical Gutzeit method may still suffers from interference of antimony. However one must consider that in this case the activity corresponding to the original antimony present in the sample is diluted by the inactive hold-back antimony carrier. In this way the active antimony that may evolve is a very small percentage of the original antimony present.

For the cases of hair analysis reported in the present paper, using the apparatus represented in Figure I, a digestion with sulfuric acid is preferable to any of the mixtures nitric-sulfuric acids, hydrogen peroxide-sulfuric acid, etc. The masses of samples to be analyzed are, in general, very small and for those samples the sulfuric acid attack has shown to be sufficient. It is possible to attack the sample in the same flask in which the arsine formation reaction is to take place latter. This avoids the additional transfer operation with eventual loss of material

on the wall of the digestion flask.

The described method was also applied to some other materials such as high purity iron and high purity magnesium<sup>(11)</sup> with equally good results. In these cases dissolution of the metallic sample has to be made with nitric acid and some drops of hydrochloric acid. Sulfuric acid is added latter and the nitric acid is evaporated. A direct attack with sulfuric acid would cause a loss of arsenic owing to the reaction of the hydrogen with arsenic, liberating arsine prematurely at the stage of dissolution of samples.

In all actual analysis (samples such as hair, filter paper, magnesium, iron) radiochemical purity of <sup>76</sup>As evolved as arsine and collected on the mercuric chloride paper, was verified by gamma spectroscopy and half-life determination (decay followed through ten half-lives). No impurities were found on the mercuric chloride paper.

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#### SUMÁRIO

Faz-se o estudo dos vários fatores que podem influenciar a recuperação de arsênico no método Gutzeit-radioquímico. Os fatores estudados foram: método de digestão da amostra, tempo de reação, concentração de ions férricos, concentração de ion estanho, interferência causada pela presença de antimônio e cobre, efeito da agitação dos frascos de reação e quantidade de arsênico-carregador necessária para boa recuperação do arsênico. A precisão e a exatidão do método são determinadas.

RÉSUMÉ

On a fait l'étude des facteurs qui ont une influence sur la récupération de l'arsenic dans la méthode d'analyse de cet élément par la technique Gutzeit-radiochimique. On a étudié le procédé pour la digestion de l'échantillon, le temps de la réaction, la concentration des ions ferriques, des ions étain, interférence de l'antimoine et du cuivre, l'effect de l'agitation des flacons de réaction et de la quantité d'arsenic entraîneur qu'on a besoin pour une bonne récupération de cet élément. La précision et l'exactitude de la méthode sont calculées.

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