



**INTERFERING ELEMENTS IN ACTIVATION ANALYSIS. STUDY OF
INSTRUMENTAL ANALYSIS POSSIBILITIES FOR THE
GROUPS: Sc-Zn. Hg-Se AND As-Sb-Br**

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INIS Categories and Descriptors

B11

B12

Activation analysis

Scandium

Zinc

Mercury

Selenium

Arsenic

Antimony

Bromine

Extraction chromatography

Ion exchange

Coprecipitation

INTERFERING ELEMENTS IN ACTIVATION ANALYSIS. STUDY OF INSTRUMENTAL ANALYSIS POSSIBILITIES FOR THE GROUPS: Sc-Zn, Hg-Se AND As-Sb-Br *

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ABSTRACT

The determination of the elements present in the groups Sc-Zn, Hg-Se and As-Sb-Br represents a classical problem in thermal neutron activation analysis, since the energy values of the gamma-ray photopeaks of the radioisotopes of these elements formed by thermal neutron activation are very close located in the spectrum.

A study is presented of the possibility of simultaneous instrumental determination of these elements by means of the spectrum stripping technique. For this purpose, artificial mixtures of the interfering elements, in varying proportions, were prepared.

Radiochemical separations procedures for the above mentioned elements were also studied by means of tracers.

INTRODUCTION

One of the most serious problems in instrumental activation analysis arises from the interferences. Among these, it must be pointed out the interference which occurs when the gamma-rays emitted by two or more radioisotopes give rise to very close photopeaks in the spectrum.

In this work, an investigation about this particular type of interference, which often happens in instrumental activation analysis, was undertaken since the gamma-ray spectrum of many radioisotopes shows more than one photopeak and sometimes a great number of them.

When only Geiger-Müller counters were available, multielementar activation analysis required radiochemical separations for each element. Later on, with the introduction of the NaI(Tl) scintillation detectors, it was possible, sometimes, to perform instrumental analyses. The spectrum stripping technique⁽¹⁾ was then introduced to improve the performance of instrumental activation analyses, since, by means of this technique, the complex spectrum may be reduced until the photopeak of interest is free from interfering activities.

However, the greatest progress of instrumental neutron activation analysis took place with the introduction of the solid state detectors. Their resolution, being very higher than that of the NaI(Tl) scintillation detectors, led the radiochemists to believe on the prevailing of instrumental activation analysis and consequently on the possibility of discarding radiochemical separations. Nevertheless, in

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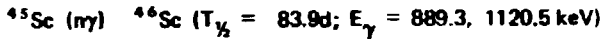
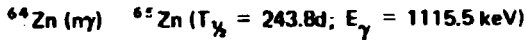
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spite of the very high Ge-Li detectors resolution, there are many cases to whose solution, radiochemical separations of groups of elements or even individual separations are necessary.

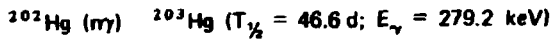
Group separations are not enough when, at least, two elements which give rise to radioisotopes whose gamma-ray spectra present photopeaks of almost the same energies are present in the group.

The groups of elements Sc-Zn, Hg-Se and As-Sb-Br are typical examples of this problem, since, by neutron activation, they give rise to the following nuclear reactions:

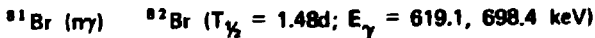
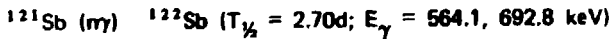
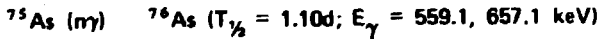
a) Sc-Zn group



b) Hg-Se group



c) As-Sb-Br group



The purpose of this work is to establish the errors on accuracy and precision of results when the cited elements are present in mixtures in several proportions, and are to be analysed by instrumental activation analysis. The visual spectrum stripping technique was used in order to minimize the influence of the interfering photopeaks.

It must be kept in mind that radioactivity is a random phenomenon which follows the Poisson's distribution. Therefore, the standard deviation of the counting value N_i at the i^{th} channel of the multichannel analyser is $\sqrt{N_i}$.

Throughout the stripping operation, an additional statistical error is introduced in the remaining spectrum. Consequently, the stripping technique has a limitation which depends on the ratio between the heights of the photopeaks that are to be subtracted and also on their energies.

Taking into account the limitations of the instrumental activation analysis for the elements studied in this work, some radiochemical separations were also applied. Scandium was separated from zinc by extraction chromatography by using tributylphosphate as complexant, since it was already shown^(3,4,7) that retention of scandium from HCl medium is almost complete, when that complexant is used.

The separation of mercury from selenium was accomplished by ion exchange, by means of an anionic resin in the sulphate form, and employing the conditions indicated by Miyamaru and Lima⁽²⁾. Arsenium and antimony were separated from bromine by coprecipitation with ferric hydroxide, according to the technique used by Vasconcellos⁽⁶⁾. Then, arsenium was separated from antimony by

means of an anionic resin in the chloride form as it was shown by Samsah⁽¹⁵⁾ and also applied by Miyamaru and Lima⁽²⁾.

INTERFERENCES IN THE GAMMA RAY SPECTRUM

a) Sc-Zn group

The gamma-ray spectrum of ^{65}Zn shows a single photopeak at 1115.5 keV, whose intensity is low, because of the poor nuclear characteristics of the isotopes involved in the (n γ) reaction. It is possible, sometimes, to determine zinc through the activity of $^{69\text{m}}\text{Zn}$ ($E_{\gamma} = 439$ keV). However, the cross-section of ^{68}Zn for the (n γ) reaction is very low and the half-life of the $^{69\text{m}}\text{Zn}$ is not long enough ($T_{1/2} = 13.9$ h) to wait for the decay of the interfering activities. Hence, the only possibility for activation analysis of zinc is, often, through the activity of ^{65}Zn . The presence of scandium in the sample to be analysed is a serious interference, because of the 1120.5 keV photopeak of ^{46}Sc . The interference will be, obviously, more or less serious, depending on the relative concentration of the target nuclides present in the sample.

b) Hg-Se group

The most suitable radioisotope of mercury for neutron activation analysis is ^{203}Hg . This radioisotope, like ^{65}Zn , shows, in its gamma-ray spectrum, a single photopeak ($E_{\gamma} = 279.2$ keV) which is overlapped by the 279.5 keV photopeak of ^{75}Se . The interference of ^{75}Se in the gamma-ray spectrum of ^{203}Hg is shown in Figure 1 and Figure 2, where it may be seen that, even when a high resolution detector is used, it is impossible to discriminate the photopeaks.

c) As-Sb-Br group

The determination of arsenium by instrumental activation analysis undergoes the interference of both antimony and bromine, since the main photopeak of ^{76}As ($E_{\gamma} = 559.1$ keV) is very close to those of ^{122}Sb ($E_{\gamma} = 564.1$ keV) and of ^{82}Br ($E_{\gamma} = 554.3$ keV). The gamma-ray spectrum of ^{76}As shows also a photopeak at 657.1 keV, but it is not useful for trace determinations of arsenium, because of its low intensity.

Since ^{76}As is shorter-lived than ^{82}Br and ^{122}Sb , the gamma-ray spectrum of an irradiated sample must be recorded as soon as possible after the irradiations in order to obtain the greater ratio between the areas of the photopeaks. This is an unfavourable condition for instrumental activation analysis since, often, it is necessary to wait for the decay of the matrix or the short-lived radioisotopes formed.

The interference of ^{122}Sb on the gamma-ray spectrum of ^{76}As is illustrated by Figures 3 and 4, where it is shown also that the interference may be minimized, but not excluded, if a high-resolution detector is used.

EXPERIMENTAL

1 - Instrumental Activation Analysis

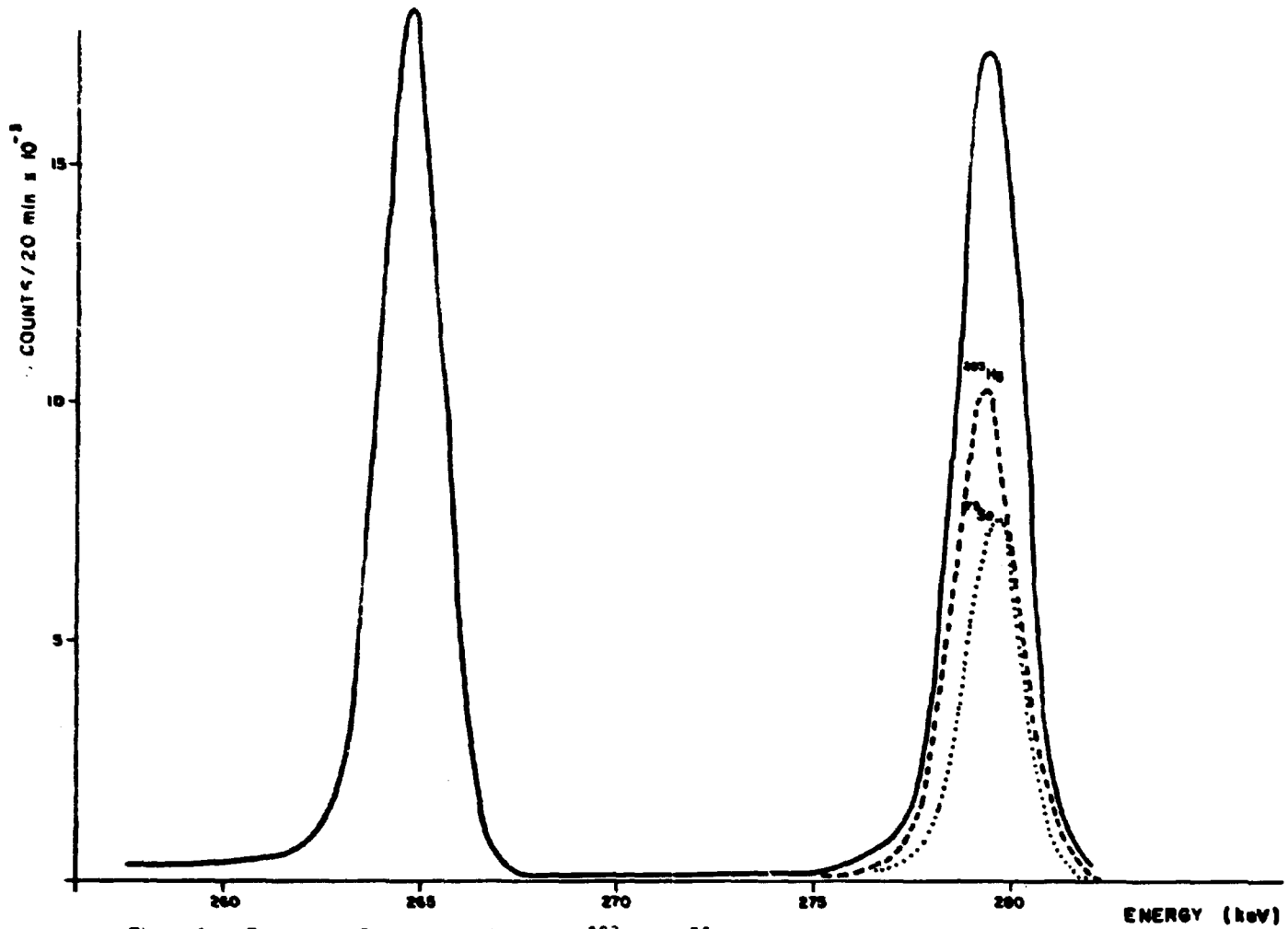


Figure 1 - Gamma-rays Spectrum of a Mixture of ^{203}Hg and ^{76}Se . Resolution of Ge-Li Detector: 3.0 keV

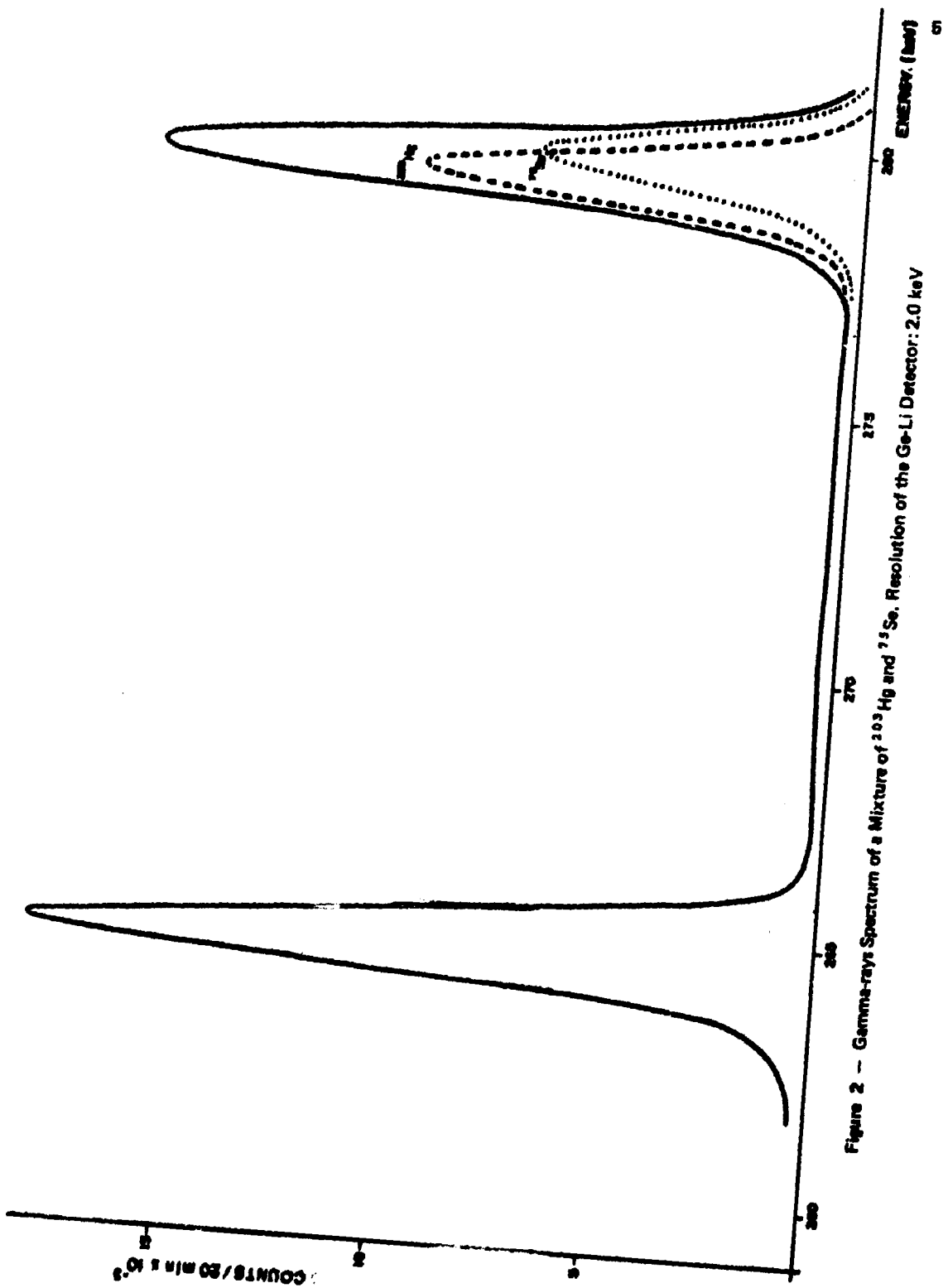


Figure 2 - Gamma-rays Spectrum of a Mixture of ^{203}Hg and ^{75}Se . Resolution of the Ge-Li Detector: 2.0 keV

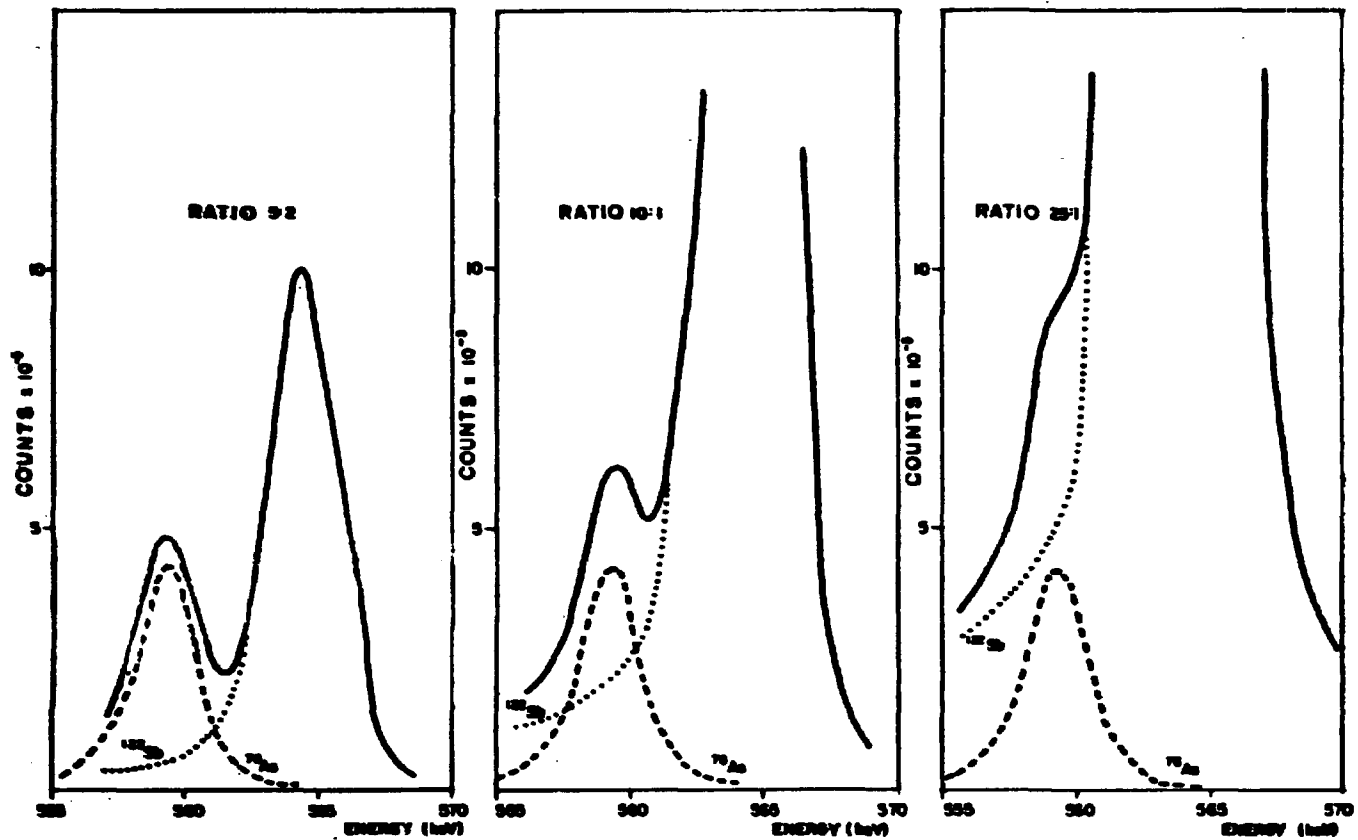


Figure 3 — Interference of Increasing Activities of ¹²²Sb on the ⁷⁶As Gamma-rays Spectrum. Resolution of the Ge-Li Detector: 3.0 keV

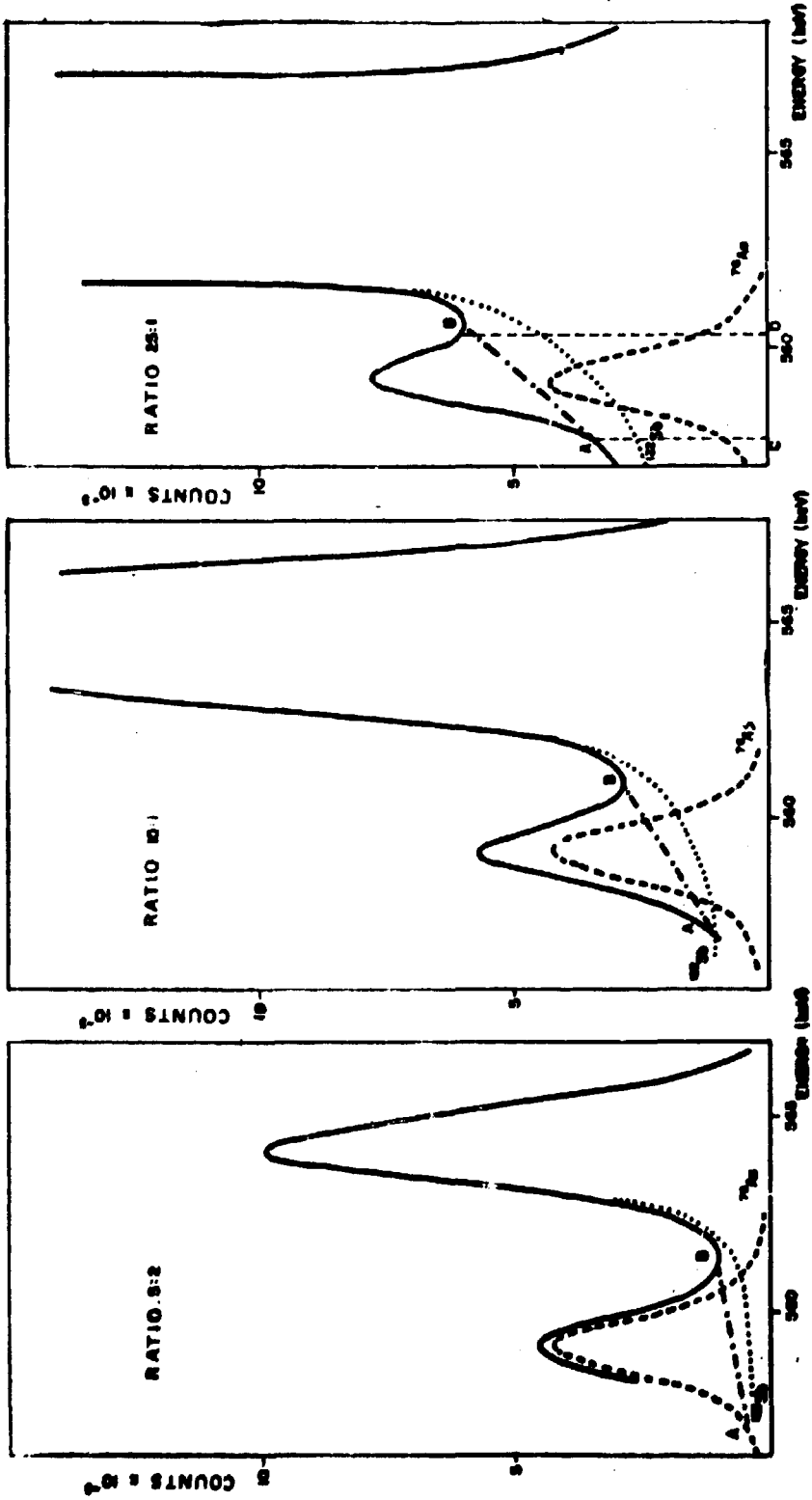


Figure 4 - Interference of Increasing Activities of ¹²²Sb on the ⁷⁶As Gamma-rays Spectrum. Resolution of the Ge-Li Detector: 2.0 keV

Apparatus

- 1 – TMC Model 404-6, 400-channel analyser coupled to a well type 7.5 x 7.5 cm NaI(Tl) scintillation detector.
- 2 – Nuclear Chicago, 4096-channel analyser coupled to a coaxial Ge-Li detector, Model 8001-0424. The energy resolution of the system was 3.0 keV (fwhm) for the 1332 keV line of ^{60}Co .

Preparation of Tracer Solutions

The elements or their oxides, after an irradiation period of 8 hours in a thermal neutron flux of $10^{12} \text{ n cm}^{-2} \text{ sec}^{-1}$, were dissolved with suitable reagents. The solutions were then diluted with deionized water.

Mercury and selenium tracers were prepared by irradiation of HgNO_3 and H_2SeO_3 solutions placed in sealed quartz vials.

Preparation of the Radioisotopes Mixtures

The mixtures were prepared directly in the counting tubes. A fixed amount of the tracer of the element to be analysed was added to several tubes. One of them was kept as standard. Increasing amounts of the interfering radioisotope were added to the former tracer in the other tubes. Besides that, a counting tube containing only the interfering tracer was prepared, in order to be used in the spectrum stripping operation.

Spectrum Stripping Technique

The spectrum stripping was performed by storing the complex spectrum in the multichannel analyser, what was followed by the visual subtraction of the interfering spectrum on the oscilloscope. The subtraction was made by taking as reference the disappearance of a second photopeak of the gamma-ray spectrum of the interfering radioisotope. The area of the photopeak of interest in the stripped spectrum was compared to the area of the corresponding photopeak of the standard spectrum. By means of the equation:

$$m = m_p \frac{C}{C_p}$$

where:

m_p = amount of the element M in the standard;

C_p = counting-rate of the radioisotope M^* in m_p ;

C = counting-rate of M^* in the mixture, after the interference subtraction; it is possible to find the amount m of element M in the mixture.

The mean value \bar{m} , the standard deviation s and the mean error E_m were calculated by means of n determinations of m .

The percentual mean error was defined by the following relation:

$$E_m = \frac{|\bar{m} - \mu|}{\bar{m}} \cdot 100$$

where μ is the true value of m .

a) Application of Mixtures of ^{46}Sc and ^{65}Zn

In order to verify the extension of the errors that may be expected in the determination of zinc, when the irradiated sample contains scandium, the activity of ^{65}Zn was fixed and then increasing activities of ^{46}Sc were added to it. The 889.3 keV photopeak of ^{46}Sc was used as reference for the visual subtraction. Results are shown in Table I.

Table I
Results for Instrumental Activation Analysis of Zn After
the ^{46}Sc Spectrum Stripping

Sc added (μg)	Zn added (μg)	NaI (TI) detector		Ge-Li detector	
		Zn Found (μg)	Mean error (%)	Zn Found (μg)	Mean error (%)
0.13	46.2	48.0 \pm 1.0	1.0	40.5 \pm 6.0	12.3
0.32	46.2	47.7 \pm 0.6	0.6	38.4 \pm 6.9	16.9
0.64	46.2	46.1 \pm 2.4	2.4	40.6 \pm 6.9	12.1
0.96	46.2	46.2 \pm 3.9	3.9	36.0 \pm 3.6	22.1
1.28	46.2	45.2 \pm 5.2	5.2	30.1 \pm 6.5	34.0

Means and standard-deviations for five determinations.

Since the 889.3 keV photopeak of ^{46}Sc falls on the same point as does the Compton edge of ^{65}Zn spectrum, the interference of zinc in the determination of scandium seemed also to be possible. Experiments were made by adding increasing activities of ^{65}Zn to a fixed activity of ^{46}Sc to confirm this supposition.

The stripping technique was not applied in this case since the gamma-ray spectrum of ^{65}Zn does not show a second photopeak to be used as reference. Results of this series of experiments are presented in Tables II and III.

Table II

Interference of the ^{65}Zn Compton Edge on the 889.3 keV
Photopeak of ^{46}Sc – Detector: NaI(Tl)

Zn added (μg)	Sc added (μg)	Sc found (μg)	Mean error (%)
46.2	0.13	0.12	7.7
115.5	0.13	0.13	0.0
231.0	0.13	0.15	15.4
462.0	0.13	0.16	23.1

Table III

Interference of the ^{65}Zn Compton Edge on the 889.3 keV
Photopeak of ^{46}Sc – Detector: Ge-Li

Zn added (mg)	Sc added (μg)	Sc found (μg)	Mean error (%)
0.235	0.64	0.66	3.1
0.462	0.64	0.63	1.6
1.155	0.64	0.63	1.6
2.310	0.64	0.62	3.1

b) Application to Mixtures of ^{203}Hg and ^{75}Se

The interference of selenium in the determination of mercury was studied by increasing the activity of ^{75}Se with respect to the fixed activity of ^{203}Hg . The reference photopeak used for the subtraction of the ^{75}Se spectrum was that of 135.9 keV. Results are shown in Tables IV and V.

Table IV

Results for Instrumental Activation Analysis of Hg, Through the Activity of ^{203}Hg , after the ^{75}Se Spectrum Stripping
Detector: NaI(Tl)

Se added (μg)	Hg added (μg)	Hg found (μg)	Mean error (%)
5.0	1.0	1.01 ± 0.02	1.0
10.0	1.0	1.04 ± 0.02	4.0
20.0	1.0	0.89 ± 0.01	11.0
30.0	1.0	0.88 ± 0.04	12.0
50.0	1.0	0.82 ± 0.08	18.0
100.0	1.0	0.69 ± 0.07	31.0

Means and standard-deviations for five determinations.

Table V

Results for Instrumental Activation Analysis of Hg Through the Activity of ^{203}Hg , after the ^{75}Se Spectrum Stripping
Detector: Ge-Li

Se added (μg)	Hg added (μg)	Hg found (μg)	Mean error (%)
42.5	16.0	16.5	3.1
85.0	16.0	15.0	6.2
170.0	16.0	15.0	6.2
260.0	16.0	13.5	15.6
340.0	16.0	12.8	20.0
430.0	16.0	12.1	24.4

Means and standard-deviations for five determinations.

c) Application to Mixtures of ^{76}As and ^{122}Sb

The simultaneous interference of ^{82}Br and ^{122}Sb on the ^{76}As spectrum was not studied since a double stripping would induced to larger error than a single one, in the analytical results.

The use of the NaI(Tl) scintillation detector, to the study of the $^{76}\text{As} - ^{122}\text{Sb}$ pair was not possible, since the reference photopeaks (675.1 keV of ^{76}As and 692.8 keV of ^{122}Sb) appear superposed in the gamma-ray spectrum.

The stripping of the ^{122}Sb spectrum from the complex one, was not possible even by using the Ge-Li detector because the reference photopeak that would be used for the ^{122}Sb subtraction has a very low intensity.

The reverse procedure, namely, the subtraction of ^{76}As spectrum from the composed one, was therefore adopted. Table VI shows the results obtained.

Table VI

Results for Instrumental Activation Analysis of Sb, Through the Activity of ^{122}Sb , after the ^{76}As Spectrum Stripping.
Detector: Ge-Li

As added (μg)	Sb added (μg)	R ^(*) As:Sb	Sb found (μg)	Mean error (%)
2.96	3.90	1:1	3.67 ± 0.15	5.9
8.30	3.30	3:1	3.27 ± 0.18	0.9
29.64	5.61	5:1	5.21 ± 0.55	7.1
7.41	0.85	9:1	0.98 ± 0.19	15.3
25.37	2.40	11:1	2.11 ± 0.28	21.1

Means and standard-deviations for five determinations.

(*) Ratio between the areas of the photopeaks of ^{76}As and ^{122}Sb .

d) Application to Mixtures of ^{82}Br and ^{76}As

The same study was applied to mixtures of ^{82}Br and ^{76}As . The 619.1 keV photopeak of ^{82}Br was used as reference for the stripping of the ^{82}Br activity. Results are presented in Tables VII and VIII.

Table VII

Results for Instrumental Activation Analysis of As, Through the Activity of ^{76}As , after ^{82}Br Spectrum Stripping
Detector: NaI(Tl)

Br added (μg)	As added (μg)	R ^(*) Br:As	As found (μg)	Mean error (%)
26.08	1.43	1:1	1.43 ± 0.03	0
35.94	0.78	3:1	0.70 ± 0.02	10.3
40.26	0.45	5:1	0.35 ± 0.06	22.2
10.49	0.069	9:1	0.056 ± 0.010	4.4
15.20	0.034	25:1	0.031 ± 0.016	8.2

Means and standard-deviations for five determinations.

(*) Ratio between the 554 keV photopeak of ^{82}Br and the 559 keV photopeak of ^{76}As .

Table VIII

Results for Instrumental Activation Analysis of As, Through the Activity of ^{76}As , after the ^{82}Br Spectrum: Stripping Detector: Ge-Li

Br added (μg)	As added (μg)	R ^(*) Br:As	As found (μg)	Mean error (%)
22.3	0.68	1:1	0.58 \pm 0.02	14.7
55.9	0.38	5:1	0.36 \pm 0.00	5.3
12.4	0.049	9:1	0.047 \pm 0.011	4.1
202.1	0.57	12:1	0.60 \pm 0.23	5.3
99.5	0.17	20:1	0.14 \pm 0.04	17.7

Means and standard-deviation for five determinations.

(*) Ratio between the 554 keV photopeak of ^{82}Br and the 559 keV photopeak of ^{76}As .

II - Activation Analysis with Chemical Separations

Apparatus

Nuclear Chicago single-channel analyser, Model 8775, coupled to a well-type 5.0 x 4.4 cm NaI(Tl) scintillation detector.

Reagents

Besides the usual chemical reagents, the following were also used:

Kieselguhr silanized Merck - grains of 0,2 to 0,3 mm.

Tributylphosphate (TBP).

Anionic Resin Amberlite CG-400 - Type I - 100-200 mesh.

Anionic Resin Bio Rad Ag-2 x 8 - 100-200 mesh.

All the reagents used in this work were of analytical grade and deionized water was used throughout the chemical separations.

Procedure

In order to avoid the peculiar interferences among the radioisotopes studied in this paper, the experiments were carried out with a single radioactive tracer each time, for the determination of the separation yields.

a) Separation of Scandium from Zinc

The extraction chromatography technique was applied for separating scandium from zinc. Use was made of silanized kieselguhr impregnated with TBP (ratio 1:1) and 8N HCl solution was used as mobile phase.

The experimental conditions were the same applied by Vasconcellos and Lima⁽¹⁷⁾ for activation analyses of minerals. Results for the separation yields between scandium and zinc are presented on Table IX.

b) Separation of Selenium from Mercury

Selenium was separated from mercury by an anion exchanger (Amberlite CG-400) in the sulphate form. The conditions applied were the same as those studied by Miyamaru and Lima⁽²⁾ for analysis of aerosol particles.

Mercury is retained by the exchanger and selenium is almost quantitatively recovered from the effluent.

Mercury may be eluted from the column by means of 0.1N HCl solution.

Results are shown in Table X.

c) Separation of Bromine from Arsenium and Antimony

The separation of bromine from arsenium and antimony was achieved by means of the coprecipitation of the latter two elements with $\text{Fe}(\text{OH})_3$. Only the carriers of bromine and iron (10 mg of each) were added before the precipitation of $\text{Fe}(\text{OH})_3$ with ammonium hydroxide. Bromine was quantitatively recovered from the filtrate through precipitation as AgBr . Table XI shows the behaviour of bromine, arsenium and antimony, even though the experiments had been made independently one from another.

d) Separation of Arsenium from Antimony

The separation of arsenium from antimony was obtained by means of an anion exchanger (Bio-Rad Ag-2 x 8) in the chloride form. The conditions were the same as those applied by Miyamaru and Lima⁽²⁾. The yield of retention of antimony by the exchanger was calculated through the activity of ^{122}Sb present in the exchanger and also in the effluent from the column. The same procedure was separately investigated for examining the behaviour of arsenium through the activity of ^{76}As . Results for separations of arsenium from antimony are shown in Table XII.

DISCUSSION

The study performed in this work allows an objective estimation of the spectrum stripping possibilities in instrumental activation analysis.

The behaviour of the stripping method differs according to the spectrum shape, as it may be seen from the results obtained for the elements analysed.

Table IX
Behaviour of Sc and Zn in Kieselguhr Imoregnated with TBP

Experiment	Sc		Zn	
	Retention (%)	Effluent (%)	Retention (%)	Effluent (%)
1	91.0	0.8	0.5	99.5
2	94.7	1.0	1.6	101.1
3	92.9	3.7	1.4	100.8
4	92.6	0.1	1.0	98.9
5	93.4	0.6	1.0	98.4
Mean and Std. Dev.	92.9 ± 1.3	1.2 ± 1.4	1.1 ± 0.4	99.7 ± 1.2

Table X
Behaviour of Se and Hg in an Ion Exchanger in the Sulphate Form

Experiment	Hg		Sc	
	Retention (%)	Effluent (%)	Retention (%)	Effluent (%)
1	101.1	0.5	1.0	102.3
2	100.8	0.0	1.1	101.8
3	101.4	0.3	1.6	101.3
4	98.5	0.9	1.0	98.9
5	99.8	1.2	0.9	97.6
6	101.5	0.0	—	—
Mean and Std. Dev.	100.5 ± 1.1	0.5 ± 0.5	1.1 ± 0.3	100.2 ± 1.9

Table XI
Coprecipitation of As, Sb and Br with Fe(OH)₃

Experiment	As		Sb		Br	
	Coprec. (%)	Filtrate (%)	Coprec. (%)	Filtrate (%)	Coprec. (%)	Filtrate (%)
1	97.5	1.9	102.8	1.0	0.1	101.3
2	96.3	2.3	98.8	3.2	0.2	101.1
3	98.8	1.4	96.3	2.0	0.1	99.7
4	102.0	1.4	104.9	0.6	0.2	101.5
5	94.6	2.7	102.6	0.0	0.1	100.8
Mean and	97.8 ± 2.8	1.9 ± 0.6	101.1 ± 3.5	1.4 ± 1.2	0.14 ± 0.05	100.9 ± 0.7
Std. Dev.						

Table XII
Behaviour of As and Sb in an Ion Exchanger in the Chloride Form.

Experiment	As		Sb	
	Retention (%)	Effluent (%)	Retention (%)	Effluent (%)
1	1.1	98.4	96.9	0.6
2	1.7	100.1	98.8	0.3
3	1.6	99.2	97.7	0.7
4	3.1	100.3	98.6	0.9
5	1.9	101.0	(*)	(*)
Mean and	1.9 ± 0.7	99.8 ± 0.8	98.0 ± 0.9	0.6 ± 0.3
Std. Dev.				

(*) Experiment lost.

Results of Table I show that the stripping of ^{46}Sc spectrum can be done when analysis of zinc through the activity of ^{65}Zn , are required. The good reproducibility of the results may be explained by the well defined reference photopeak of ^{46}Sc . It may be seen that by using a NaI(Tl) scintillation detector the precision and accuracy of results is better than when a Ge-Li detector was used. The higher efficiency of the former probably helps the spectrum stripping operation in minimizing the additional error introduced by the subtraction operation.

It may also be seen, from Tables II and III that the Compton edge of the ^{65}Zn spectrum has practically no influence on the 889.3 keV photopeak of the ^{46}Sc when a Ge-Li detector is used.

The error must be taken into account only when there is a great disproportion between the amounts of zinc and scandium in the sample and this, even when a NaI(Tl) scintillation detector is used.

The method proposed for chemical separation of scandium from zinc is fast and simple and gives a good reproducibility as it may be seen from results shown in Table IX.

For mercury and selenium (Tables IV and V) the percentual mean error increase with the increasing ratio between the amounts of selenium and mercury in the sample. If errors of about 10% in the accuracy of results are allowable, the stripping technique may be used, when the ratio between selenium and mercury amounts is of nearly 30. This ratio must be reduced by a factor of two if a Ge-Li detector, instead of the NaI(Tl) scintillation detector, is used. Again, the latter seems to give a better performance for the spectrum stripping technique.

The chemical separation proposed for selenium and mercury is simple and gives very good results as it may be seen from results presented in Table X.

Concerning the instrumental activation analysis of arsenium and antimony, the problem becomes more difficult, because the NaI(Tl) scintillation detector cannot be used for the stripping technique. Even using a Ge-Li detector, the results show a poor reproducibility, when the ratio between the activities of ^{75}As and ^{122}Sb is greater than 10 (Table VI). Several results for the same sample are required in order to have a mean value that may be taken as representative of the real one.

For the mixture of ^{82}Br and ^{76}As the percentual mean error shows random values (Table VII), namely, there is not a logical agreement between the increasing of the percentual mean error and the increasing of the ratio between the ^{82}Br and ^{76}As activities. This proves, the doubtfulness of the stripping technique, because of the subjectivity of the visual operation. The results obtained with the Ge-Li detector (Table VIII) lead to the same conclusion. From these results it may be inferred that instrumental activation analysis of arsenium, when bromine or antimony are present in the sample, may conduct to inadmissible analytical errors.

The separation of arsenium and antimony from bromide by coprecipitation with ferric hydroxide is almost complete as it is shown by results presented in Table XI. The loss of antimony and arsenium in the filtrate is negligible, mainly in the case of trace analyses.

The retention of antimony as a chloro-complex by an anion exchanger allows a good decontamination from arsenium (Table XII), by means of a fast radiochemical separation.

It must be pointed out that the study developed in this work was limited to a certain range of activities ratios. In spite of the fact that the stripping technique had been acceptable for ^{46}Sc and ^{65}Zn mixtures, it is probable that the errors will be increased with increasing ^{46}Sc activities.

However, it must be recognized that a better resolution of the detector will improve the instrumental analysis as it may be seen in Figure 1 and 2. Nevertheless, there are some problems of spectrum interferences, for instance, the case of ^{75}Se and ^{203}Hg , which cannot be solved by improvements in the detector resolution.

RESUMO

A determinação dos elementos presentes nos grupos Sc-Zn, Hg-Se e As-Sb-Br constitui um problema clássico em análise por ativação com nêutrons, já que os radioisótopos formados apresentam fotopicos em energias muito próximas no espectro de raios gama.

Faz-se, no presente trabalho, um estudo da possibilidade de determinação instrumental desses elementos por meio da técnica de subtração de espectros. Para esse estudo, prepararam-se misturas artificiais dos elementos interferentes, em proporções variadas.

Estudaram-se também separações radioquímicas para os elementos mencionados acima, por meio de traçadores.

REFERENCES*

1. DE SOETE, D.; GIJBELS, R.; HOSTE, J. *Neutron activation analysis*. London, Wiley, 1972. p.406-44. (Chemical Analysis: A series of monographs on analytical chemistry and its applications, 34).
2. MIYAMARU, M. & LIMA, F. W. Aplicação do método de análise por ativação à determinação de poluentes atmosféricos. *Revta. bras. Tecnol.*, 4:133-40, 1973.
3. MORRISON, G. H.; GERARD, J. T.; TRAVESI, A.; CURRIE, R. L.; PETERSON, S. F.; POTTER, N. M. Multielement neutron activation analysis of rock using chemical group separation and high resolution gamma spectrometry. *Analyt. Chem.*, 41(12):1633-7, 1969.
4. PEPPARD, D. F.; FARIS, J. P. GRAY, P. R.; MASON, G. W. Studies of the solvent extraction behaviour of the transition elements. I. Order and degree of fractionation of the trivalent rare earths. *J. phys. Chem. (Easton)*. 57(3):294-301, 1953.
5. SAMSAHL, K. Radiochemical method for determination of arsenic, bromine, mercury, antimony and selenium in neutron-irradiated biological materials. *Analyt. Chem.*, 39(12):1480-3, 1967.
6. VASCONCELLOS, M. B. A. *Coprecipitação com hidróxido férrico: aplicação à separação de cobre e arsênio e de arsênio e antimônio*. São Paulo, 1972. (Dissertação de mestrado, Instituto de Química, Universidade de São Paulo).
7. VASCONCELLOS, M. B. A. & LIMA, F. W. Activation analysis of alkaline rocks. A comparison of the destructive and non-destructive methods. *J. radioanal. Chem.*, 44:55-81, 1978.

(*) As referências bibliográficas relativas a documentos localizados pelo IEA foram revistas e enquadradas na NB-66 da ABNT.

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