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ACTIVATION ANALYSIS OF CHROMIUM IN WATER MATRIX

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Chromium at concentrations of parts per billion in water, may be determined by activation analysis using an instrumental method preceded by concentration on anion exchange resins. Blank runs, using deionized water, are carried through the steps of preconcentration. The blank-resin and sample-resin are irradiated together with thermal neutrons, and the gamma spectrum of each is stored in half of the memory unit of a multichannel analyzer. Subtraction of the blank-resin spectrum from the sample-resin spectrum gives the ^{51}Cr peak free from interfering activities.

Introduction

In trace analysis, the trace element to be analyzed occurs, in general, together with other elements of about the same concentration, and all traces are dispersed in a matrix which consists of elements that are present in the largest proportion in the mixture. The concentration of the trace elements are in the range of parts per million or parts per billion, and the absolute quantities in the range of micrograms or less.

As a consequence of this disproportion in the quantities of matrix and trace elements, the analysis of traces is usually complicated by interference caused by the matrix, especially when purely instrumental methods, without chemical separations, are used. Matrix interference is enhanced when highly sensitive methods of analysis are employed as in the case of activation analysis, when the activity induced in the matrix owing to its large mass is much higher than the activity of the trace element to be analyzed.

In many cases the matrix consists of elements having low cross sections for the activation reaction. Solutions in water or organic solvents are examples of low cross section matrices, and constitute cases in which direct irradiation of the matrix containing the trace elements to be determined may be considered. However, low concentration of the trace element in the organic or in the water solutions requires the handling and irradiation of large volumes of liquids and this gives rise to further complications, especially in connection with irradiation problems. For these types of matrices a preconcentration or enrichment step is almost invariably essential. However, in many cases of activation analysis, preconcentration operations are hampered by problems of contamination of the samples, or by the risk of losses of trace elements.

Contamination problems cannot always be avoided, since, at trace levels, vessels, reagents, etc. may also introduce amounts of trace elements of the same order of magnitude as the one to be determined. In some cases blank runs carried through all steps of the actual separation may help to overcome the complications introduced by such sources of contamination.

Loss of trace elements is also an ever present and troublesome problem in connection with trace analysis, and the lower the concentration of trace, the higher are the chances of loss. Problems involved in the preconcentration operations can be overcome by choosing appropriate techniques and convenient sample size, and balancing them judiciously in order to make the enrichment or preconcentration of the trace a simple operation. Very complex techniques and very large samples should be avoided whenever possible. A thorough examination of problems in connection with preconcentration and enrichment has been made by MIZUIKE.[1]

Analysis of chromium

In the course of a study of hydrology problems concerning the localization of leakages in dams, chromate was used as a stable tracer. Samples of the collected water had to be analyzed for chromium present at the level of parts per billion. Other elements present were sodium, calcium and silicon.

Of the many preconcentration techniques, the use of anion exchangers seemed to be suitable to solve this problem, since most of the potential interfering substances were present as cations. The use of ion exchanger resins also permits the duplication of operations for blank runs in a very simple manner.

After chromium, as chromate, has been absorbed by the resin from the solution passed through it, this resin and blank ones are irradiated directly, and their activities determined in a multichannel analyzer. The spectrum of the blank-resin is stored in one half of the memory unit of the analyzer, and that of the sample-resin in the other half. Subtraction of the blank spectrum from the sample spectrum makes it possible to use chemical operations only at the beginning of the process, when oxidation of traces of chromium in the water is accomplished by means of hydrogen peroxide. In this way contamination by reagents can be practically avoided. Interference from other anionic species absorbed by the resin can be eliminated by choosing appropriate cooling times before counting the sample and blank resins. Losses of chromium owing to its very low concentration were investigated by means of ^{51}Cr solutions in concentrations from about one part per million down to one part per billion of chromate ion, and it was shown that in this concentration range the recovery of added chromium was higher than 99%.

The use of resins for chromate retention and colorimetric determination of chromium in alkali hydroxides at submicrogram level has been reported by MANNING, MILLER and ROWAN.[2]

Experimental

Materials and reagents

Glass columns of 0.5 cm diameter and 5 cm length were used. As anion exchanger, Amberlite *IR*-401, 50–100 mesh (0.5 g of exchanger per column) was employed. The ion exchanger was converted into hydroxide form with 2 *M* NaOH solution, and washed with deionized water.

Hydrogen peroxide, 130 volumes.

Ammonium hydroxide solution (28% NH_3).

Potassium bichromate standard solutions containing 20 and 50 μg of chromium per ml.

Potassium chromate solution containing 10 mg of chromium per ml.

Iron (III) chloride solution containing 10 mg of iron per ml.

Barium chloride solution (10%).

Acetic acid solution (6 *M*).

Ammonium acetate solution (6 *M*).

Polyethylene envelopes for sample irradiation, 2 × 4 cm.

All chemicals were of analytical grade purity.

Method

To a volume of 2500 ml of water containing the chromium, ammonium hydroxide solution is added to adjust the *p*H to 10. The solution is boiled and 0.8 ml of hydrogen peroxide per liter of water is added. Gentle boiling is maintained for 15 minutes. After cooling to room temperature, the solution is percolated through the ion exchanger column at a rate of 2 ml per minute. Wash the column with 100 ml of deionized water. Dry the resin at about 80° C, and transfer to the polyethylene envelopes. A blank run is carried out in parallel, using the same volume of deionized water.

The sample and blank resins are irradiated together, as well as standards of 2 to 5 μg of chromium, for 8 hours in a thermal neutron flux of $5 \cdot 10^{12}$ n $\cdot$ cm^{-2} $\cdot$ $\cdot$ sec^{-1}

After a cooling period from 24 hours (for samples at parts per million level) to 70 hours (for samples at parts per billion level) the samples are counted in a multichannel analyzer (TMC-Model 404–6) coupled to NaI-Tl scintillation well crystal (13/4″ × 2″) (Harshaw).

The sample spectrum is stored in one half of the memory unit of the 400-channel analyzer and the blank spectrum in the other half. Gain values are set to give 0.01 MeV/channel. The analyzer is coupled to a TMC Resolver-Integrator, Model 522, by which the blank-spectrum can be subtracted from the sample-spectrum. The area of the peak at 0.321 MeV, after subtraction, is obtained by integration, and compared with the area of the same peak for standards of ^{51}Cr. Figures 1 and 2 are typical results for a chromium analysis in water containing 10 parts per billion of chromium. The spectra in those figures were obtained after a cooling time of 70 hours in order to show more clearly the peak at 0.321 MeV for ^{51}Cr. For calculations a cooling time of only 24 hours would be sufficient.

If the concentration of chromium in water is too low, larger volumes of water or a cooling time longer than 24 hours should be used in order that short half-life activities in the resins may decay to values that will not prevent a good resolution of the ^{51}Cr peak. Alternatively, the resin, after irradiation may be incinerated in an iron crucible at about 700° C, and residue fused with sodium peroxide at 500° C. The solid cake is dissolved in hot water and 10 mg of chromium (potassium chromate) is added as carrier. The solution is scavenged by precipitation of ferric hydroxide three times, the filtrate is made acid by adding acetic acid and ammonium acetate, chromium is precipitated as barium chromate, and counted as previously.

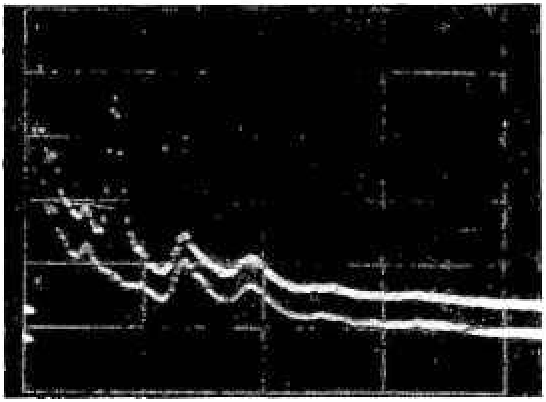

Fig. 1. Gamma spectra of sample-resin (above) and blank-resin (below)

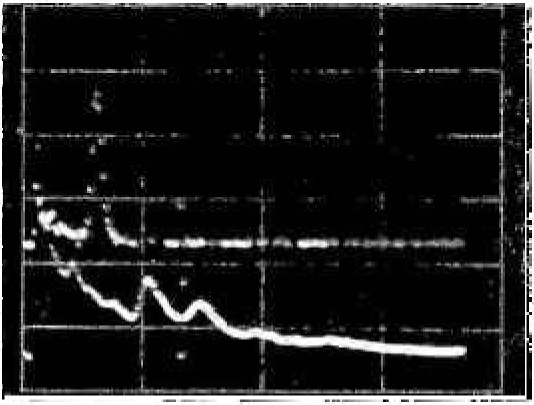

Fig. 2. Gamma spectrum of sample-resin (above) after subtraction of the spectrum of blank-resin (below)

Results and discussion

In Table 1 are reported some experimental results obtained by adding known amounts of chromium, as chromate, to deionized water.

Table 1

Determination of chromium (chromate) in water

ppb	ng of Cr		Recovery (%)
	added	found	
300	75	72.2	96
200	50	54.7	103
50	25	26.5	106
30	75	81.9	109
20	50	51.2	102
10	25	26.3	105
5	10	10	100
5	10	9.7	97
4	10	9.5	95
2.5	5	5.0	100
2.5	5	5.1	102
1.0	2.5	2.3	91
1.0	2.5	2.7	107

Blank runs were carried out in parallel using deionized water: with irradiation times of 8 hours and cooling times of 24 hours chromium has not been detected in the deionized water.

The precision of the method, expressed in terms of standard deviation, is shown in Table 2 for repeated determinations with six different samples of water.

Table 2

Precision of the determinations of chromium in water
(results in parts per billion)

Sample					
A	B	C	D	E	F
1.8	29.0	1.6	39.0	1.6	78.0
1.5	28.7	1.8	36.0	1.6	70.0
1.7		1.7	41.0	1.7	
2.0				1.7	
1.5				1.4	
1.9					
1.8					
1.9					
1.8 ± 0.2*	28.9 ± 0.2*	1.7 ± 0.1*	38 ± 3*	1.6 ± 0.1*	74 ± 6*

* Standard deviations.

Tables 1 and 2 show that the instrumental method preceded by a concentration on an anion exchanger gives good accuracy and precision down to one part per billion. For lower values of chromium concentration a longer irradiation period would be required, resulting in too high a value for the activity of the blank resin and this would mask the peak for ^{51}Cr. In such cases a longer cooling period before counting would be necessary, unless the technique of incinerating the resin is used, or a larger volume of water is percolated through the resin.

References

1. A. Mizuike, Separations and Preconcentrations. In: Trace Analysis. Physical Methods (Edited by G. H. Morrison) Interscience Publishers, New York, 1965.
2. D. L. Manning, W. K. Miller and R. Rowan, jr., ORLN—1396, 1952.

RESUMO

Cromo em concentração de partes por bilhão em água pode ser determinado por análise por ativação usando método instrumental precedido por uma concentração do anion cromato em resina aniônica.

Análises em branco, usando água desionizada, são feitas contemporâneamente durante tôda fase de pré-concentração. A resina-amostra e a resina-branco são irradiadas ao mesmo tempo com nêutrons térmicos e o espectro gama de cada são registrados em cada metade da memória de um analisador multicanal. A subtração do espectro da resina-branco do da resina-amostra, dá o pico de 0,321 Mev do cromo livre de interferências.

RÉSUME

L'analyse par activation de chromiun, en concentration correspondent à parties par billion dans l'eau, à été fait par concentration prealable dans une resine exchangeuse d'anions.

Des essays en blanc ont été fait avec de l'eau déminéralisée. La resine blanc et la resine avec le chromiun ont été irradiées au même temps et les spectro gamma accumulés dans chaque moitié de la mémoire d'un analyseur multicanal. Par soustraction du spectro de la resine blanc du spectro de la resine avec le chromiun on obtient le pic du ^{51}Cr sans intérférence d'autres activités.