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INIS Categories and Descriptors

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CHROMIUM
COBALT
FRESH WATER
ION EXCHANGE
IRON
MERCURY
NEUTRON ACTIVATION ANALYSIS
TOXICITY
ZINC

DETERMINATION OF TRACE ELEMENTS IN DRINKING WATER BY NEUTRON ACTIVATION ANALYSIS*

Casimiro Sepúlveda Munita, Rodnei Massamiti Abe **
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ABSTRACT

The concentration of Hg, Cr, Zn, Fe and Co has been de-
termined in fresh drinking water by a combination of precon
centration and neutron activation analysis. In order to pre-
concentrate the trace metals, a Chelex-100 resin in the NH_4^+-
form has been employed and it was not necessary to use special
agents for the adsorption of the elements which are practi-
cally quantitatively retained by the resin. The retention of
each element during the preconcentration was investigated
using radioactive tracers. Selenium is known as a   strongly
interferent element for the analysis since the (n,γ)produced
^{75}Se has a γ-line at 0.279 MeV which coincides with the only
γ-line of ^{203}Hg. The separation was made by a selective re-
tention of mercury. After the sample had passed through the
resin, the column was transfered to a polyethylene envelope
and irradiated at a neutron flux of about $5.10^{12}ncm^{-2}s^{-1}$ for
8 h. For Hg the resin was irradiated in quartz ampoules. The
samples were counted 15 days after the irradiation. The pre-
sent method is superior to most other Chelex-100 separation
procedures where elements of interest are eluted from   the
resin prior to their determinations thereby introducing the
possibility of additional reagent blanks and incomplete   as
well as non-reproducible recoveries.

DETERMINAÇÃO DE ELEMENTOS AO NÍVEL DE TRAÇOS EM AMOSTRAS DE ÁGUA POR ANÁLISES POR ATIVAÇÃO COM NÊUTRONS

RESUMO

Desenvolveu-se um método analítico para determinar Hg,
Cr, Zn, Fe e Co em amostras de água. O procedimento experimen
tal baseou-se na pre-concentração dos elementos de interesse

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numa resina CHELEX-100 (100-200 mesh) na forma amônio.Tomando
como base o comportamento dos íons na resina,estabeleceram-se
as condições mais favoráveis de retenção mediante o uso   de
traçadores radioativos. Estudou-se, também, o rendimento quí
mico do processo, encontrando-se um valor acima de 95%   para
os elementos envolvidos. O método analítico foi aplicado   em
amostras de água potável coletada em São Paulo.

INTRODUCTION

The determination of trace elements in natural waters is
of great importance for the control of environmental   pol-
lution. Many trace elements reach the human organism   through
water and food-chain and their determination in   drinking
water is needed. The determination of traces in water is   a
most difficult task due to the very low concentrations   of
these metals and also to the severe problems with   contami-
nation from a multitude of sources and, at the same time,seri
ous losses of metal can occur by adsorption on the walls of
sample botles or analysis vessels and considerable experience
is needed before reliable results can be obtained.The purpose
of this paper is to present a method for the determination of
Hg, Cr, Zn,Fe and Co in tap water. These elements were chosen
because some of them can be toxic such as   mercury   and
chromium. In accordance with the Brazilian laws[1] the   upper
limits for mercury and chromium are 0.2 µg/L and 0.55 µg/L,
respectively.

Although physical analysis methods providing low limits
of detection are widely used, the direct determination   of
trace elements in waters is possible only for a   restricted
number of elements[4]. Preliminary concentration enables one
to isolate the trace elements from a large volume of solution

of complex composition, and thus to reduce the limit of detection and to eliminate or substantially reduce the effects of the macroscopic components,which improves the accuracy and precision as well as sensitivity.

Various preconcentration techniques have been described in the literature: preconcentration on active carbon[14], sorption on polyurethane foams[2,13], coprecipitation with organic collect rs[10,11], lyophilization[6], solvent extraction[9] and ion exchange[7,8].

Many preconcentration methods can be used together with the determination of trace components by neutron activation analysis. It has been pointed out[12] that sorption methods are particularly convenient, especially ion exchange chromatography, as they enable one to isolate trace components in pure form. In this case, an advantage is that one irradiates the resin bearing the sorbed trace elements,which substantially reduces the effects of sample preparation on the reproducibility.

Preconcentration of trace elements in a Chelex-100 resin can be an attractive alternative to the direct neutron activation in water samples. Enrichment of the trace contituents permits the use of a large volume of water sample for analysis, thus extending the lower limit of detectability and the trace elements present as impurities in the resin become negligible as opposed to the preconcentrated elements. On the other hand, one great advantage is that the errors, which are normally introduced during sample handling, can be excluded.

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EXPERIMENTAL

Reagents

All reagents used were of analytical grade.

Solvents: tap water was first demineralized, in ion-
-exchangers resins, followed by distillation in a quartz dis-
tillator. Nitric acid and ammonia solution were also distill-
ed from quartz apparatus.

Bio-Rad Chelex-100, Na^+ - form (100-200 mesh) was washed
with distilled demineralized water. Before use, Chelex-100 was
converted to NH_4^+ - form by conventional methods.

The following radioisotopes were used as tracers: ^{203}Hg,
^{51}Cr, ^{59}Fe, ^{65}Zn, ^{75}Se and ^{60}Co.

Approximately 10 mg of each metal or metal oxide(Johnson
and Matthey "Spec.Pure") were accurately weighed,dissolved in
about 1 mL of concentrated nitric acid and finally diluted to
10 mL with distilled water.

Apparatus

A Nuclear Chicago single channel analyzer coupled to a
3.7 cm x 6.2 cm welltype NaI(Tl) crystal was used for the
measurements of the activity,when only one radioactive tracer
was involved.

For the gamma-spectra measurement a solid state Ge(Li)
detector, ORTEC, model 8001-1022V, nº 16-3911 was used. This
γ-ray spectrometer was coupled to a 4096 - multichannel analy
zer. The resolution of the detector is 2.8 keV for the 1332
keV of ^{60}Co.

The apparatus used for the radioisotope preconcentration consisted of a polyethylene column (5.0 cm long and 0.5 cm diameter). The column was joined to a glass vessel (250 mL).

Procedure

The polyethylene columns, used to hold the Chelex-100 resin were allowed to soak for one week in HNO_3 conc. before use. After rinsing with water, slurry corresponding to 1.5 mL of hydrated resin in the sodium form (about 200mg dry weight) was loaded into each column. The resin was washed with three 10 mL portions of 2 N HNO_3 to elute any trace metal contamination. Excess acid was removed by washing the resin with 10 mL of water. The resin was converted to the NH_4^+ - form by the addition of two 25 mL portions of 2 M NH_4OH. The pH of the last few drops eluted was checked using pH paper.If they were not basic, additional NH_4OH was added until a basic pH was achieved. Residual NH_4OH was removed from the resin by washing with two 5 mL water aliquots. The glass reservoir on top of the column was then filled and the sample passed through the resin at a flow rate of about 2.5 mL/min.After the sample had passed through the resin, the column was placed in a poly ethylene envelope and simultaneously irradiated with a standard at a neutron flux of about 5.10^{12} ncm^{-2} s^{-1} for 8 h. For Hg analysis the resin was irradiated in quartz ampoules. The ampoules were heat sealed while being kept in liquid nitrogen to avoid heating of the sample and losses of mercury of volatilization. Sample activities were measured 15 days after the irradiation.

RESULTS AND DISCUSSION

The retention of each element during the preconcentration was investigated using radioactive tracers. The tracers were added to 100 mL of demineralized water, then passed through the column containing Chelex-100 resin in the NH_4^+- -form, at a flow rate of 2.5 mL/min.

The resin was then transferred to a counting tube and its activity measured by means of a gamma-ray spectrometer . The retention was calculated by comparison with the activity of suitable standards prepared by placing the same amounts of the radioactive tracers. The results of the tracer studies ' are shown in Table 1.

TABLE 1 – Retention of Elements Using Chelex-100 Resin, NH_4^+ – Form

Element	Percent Retention[*]
Hg	97.0
Cr	99.3
Fe	93.0
Zn	99.9
Se	0.7
Co	99.4

[*] based on 4 measurements

The reproducibility of the elements not quantitatively retained will be sufficient to allow retention correction to be made for these elements in the real samples analysis. Selenium is known as a strongly interferent element as the (n,γ)

produced ^{75}Se has a γ-line at 0.279 MeV which coincides with the only γ-line of ^{203}Hg. The separation was made by a selective retention of mercury.

In order to preconcentrate the trace metals it was not necessary to use special agents for the adsorption of Hg, Cr, Fe, Zn and Co, which were practically quantitatively retained in their ionic forms by the resin. Large molecules and colloidal particles are not sorbed by this resin due to the small pore size of the resin bead (1.5 nm)[5]. The behaviour of the chemical yields procedure was examined by adding known amounts of Hg, Cr, Fe, Co and Zn to 200 mL of demineralized distilled water. The chemical yields were calculated by comparing the added and recovered amounts. The results for the chemical yields are shown in Table 2.

TABLE 2 - Results of the Chemical Yields by the   Proposed Procedure

Element	Recovery (%)[*]
Hg	75.5 ± 1.3
Cr	97.3 ± 2.0
Fe	90.8 ± 3.7
Co	97.9 ± 3.5
Zn	95.5 ± 5.9

[*]based on 5 measurements

Limit of determination were calculated according to the method of Currie[3], and are shown in Table 3 for a typical sample.

TABLE 3 - Determination Limits Determined Using Currie's[3] Criterion

Element	Determination Limit (μg/L)
Hg	0.07
Cr	1.4
Fe	120
Zn	5.1
Co	0.2

In order to evaluate the method, replicate analysis were carried out by the proposed procedure, for trace elements in a drinking water sample taken in the city of São Paulo. The samples were counted 15 days after irradiation to eliminate the interfering activities of ^{24}Na, ^{82}Br and ^{38}Cl. The results are shown in Table 4. The found concentration of Fe, Zn, Cr, Co and Hg were much lower than that accepted values by the Brazilian[1] and international[15] laws.

The preconcentration neutron activation analysis method developed in this study for the determination of trace elements using the Chelex-100 resin is simple and efficient. Concentrations of Hg, Cr, Fe, Co, Zn, can be routinely determined by the direct irradiation of the resin in which the elements are preconcentrated. In this respect, the present method is superior to most other Chelex-100 separation procedures where elements of interest are eluted from the resin prior to their determinations thereby introducing the possibility of additional reagent blanks and incomplete as well as non-reproducible recoveries. The resin loaded with trace elements is a near-ideal matrix for neutron activation analysis, and pro

bably for the other analytical techniques where a solid sample is more convenient to use.

TABLE 4 - Concentrations of Elements in Water Samples Collected in São Paulo

Element	Sample (µg/L)		
	1	2	3
Fe	376.6	340.2	2.9.7
Co	0.13	0.23	0.12
Zn	27.3	26.0	23.1
Cr	0.84	0.99	0.67
Hg	0.1	< 0.1	< 0.1

ACKNOWLEDGMENTS

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