Journal of Radioanalytical and Nuclear Chemistry, Articles, 88/2 (1985) 241–257

APPLICATION OF THE RADIOREAGENT METHOD FOR TRACE DETERMINATION OF LEAD*

A. M. G. FIGUEIREDO, M. SAIKI, F. W. LIMA

Radiochemistry Division, Instituto de Pesquisas Energéticas e Nucleares, Comissão Nacional de Energia Nuclear-SP, Caixa Postal 11049 (Pinheiros), São Paulo, SP (Brasil)

(Received December 1, 1983)

A radioreagent method of analysis was developed and applied to the determination of trace quantities of lead in several types of samples. The method is based on the extraction of radioactive cobalt, displaced by lead from the cobalt chelate of ethylenediaminetetraacetate labelled with ^{60}Co, into a tetracycline–benzyl alcohol solution. The radioactivity of the released cobalt, extracted into the organic phase, is proportional to the lead concentration. Interference caused by some elements was eliminated by means of a previous separation of lead using dithizone. The method was applied for lead determination in aerosol samples, gasoline and samples from the International Atomic Energy Agency, namely: simulated-air filter (Air-3), fresh water (W-3), dried animal whole blood (A-2) and calcined animal bone (A-3/1). The sensitivity, accuracy and precision of the method were also studied.

Introduction

Lead is known as one of the highly toxic element and its analysis in different types of environmental samples is of high general interest. Neutron Activation Analysis is not useful for the determination of lead because of the rather unfavourable nuclear characteristics of its isotopes for neutron irradiation. The only thermal neutron reactions of importance for lead isotopes are: ^{206}Pb(n, γ)^{207m}Pb and ^{208}Pb(n, γ)^{209}Pb. In the first reaction the ^{207m}Pb produced has a very short half-life of 0.8 sec. The reaction ^{208}Pb(n, γ)^{209}Pb is of limited use in activation analysis because the cross-section for this reaction is rather small (σ_{th} = 0.0005 barns). Besides, ^{209}Pb is a pure beta emitter and a radiochemical separation of lead would be necessary for its measurements.

*Part of this material was submitted to the University of São Paulo in partial fulfilment for a Doctor of Science's Degree of A. M. G. FIGUEIREDO.

The radioreagent method has been applied with success for determination of many elements. MENON[1] has presented a comprehensive review of the method stressing the basic requirements for its feasibility.

The radioreagent method presented in this paper for lead analysis seems to comply with the basic requirements expressed in Ref.[1] The method consists in measuring the activity of cobalt displaced by lead ion from cobalt-ethylenediaminetetraacetate labelled with ^{60}Co. The cobalt displaced is separated from the cobalt chelate (Co*-EDTA) present in the aqueous solution by means of its extraction into a tetracycline – benzyl alcohol solution. The radioactivity of the cobalt displaced is proportional to the concentration of lead in the sample.

The chemical reactions involved in the determination of traces of lead by using a solution of Co-EDTA labelled with ^{60}Co as radioreagent can be represented by the following equilibria:

$$Co^*\text{-}EDTA_{(aq)} + Pb_{(aq)} \rightleftharpoons Pb\text{-}EDTA_{(aq)} + Co^*_{(aq)} \quad (1)$$

$$Co^*_{(aq)} + n\,TC_{(org)} \rightleftharpoons Co(TC)_{n\,(org)} \quad (2)$$

in which TC represents the tetracycline molecule and the lower indexes (aq) and (org) refer to compounds present in the aqueous and organic solution, respectively. Charges are omitted for simplicity.

Since the stability constants for the lead complex and cobalt complex with ethylenediaminetetraacetic acid ($\lg K_{Pb\text{-}EDTA} = 18.04$,[2] $\lg K_{Co\text{-}EDTA} = 16.31$[3] differ by about one hundred units, the reaction represented by Eq. (1) may be used to determine lead. This reaction is complete in a very short time.

The extraction of the cobalt displaced by lead in Eq. (1) could be carried out by dithizone or by 2-nitroso-1-naphthol in chloroform or carbon tetrachloride, for instance. However, the extraction reaction of cobalt with dithizone-carbon tetrachloride takes more than an hour,[4] being slower than with TC – benzyl alcohol whose extraction equilibrium is attained in less than 5 min. The extraction of cobalt with 2-nitroso-1-naphthol is not useful in this case since nitrosonaphthol forms with Co^{2+}, Co^{3+} and Pb^{2+} complexes that are more stable than the complexes of the same elements with EDTA.

Properties of the antibiotic tetracycline(TC) as complexing agent in solvent extraction of many elements have been studied in our laboratory.[5] The extraction parameters using TC in benzyl alcohol solution such as extraction curves, types of complexes formed and extracted, masking reagents for interfering reactions for the complexes formed have been determined for several elements.[5] Stability constants were determined for Th-TC and lanthanide-TC complexes.

The solution of tetracycline in benzyl alcohol is a good extractant for cobalt, complete extraction occurring at pH 4.0 and up. There is no displacement of Co* from the Co*-EDTA complex, promoted directly by TC, since the stability constant of Co–EDTA is higher than the one of Co-TC complex ($\lg \beta_2 = 9.80$ for Co-TC[2]). This means that all displaced cobalt appearing in the aqueous solution will be originating in reaction (1), being proportional to the amount of lead being analyzed. Also, the reaction between TC and Pb of Pb-EDTA complex does not take place since the stability constant for the Pb-TC complex ($\lg \beta_2 = 6.59$[6]) is smaller than the one for Pb-EDTA ($\lg K_{Pb\text{-}EDTA} = 18.04$). In the presence of the interfering elements lead is first separated using dithizone[4] and then determined by the procedure reported here.

To study the general applicability of the present method, lead content was determined in several samples such as airborne particulates, gasoline and samples provided by the International Atomic Energy Agency (IAEA), namely: simulated-air filters (Air-3), fresh water (W-3), dried animal whole blood (A-2) and calcined animal bone (A-3/1).

Experimental

Equipment

A single channel gamma-ray spectrometer coupled to a 5.1 cm × 4.5 cm NaI(Tl) well-type scintillation detector was used to measure the activity of ^{60}Co.

Preparation of solutions

All chemicals used were of analytical grade. Deionized water was distilled in a quartz apparatus and used throughout.

A solution of $5 \cdot 10^{-3}$ M lead nitrate was prepared by dissolving lead nitrate with water. Cobalt solution with the concentration of $4.0 \cdot 10^{-2}$ M was prepared dissolving basic cobalt carbonate with a hot dilute hydrochloric acid solution. Solutions of lead and cobalt were standardized by titration with a primary solution of disodium ethylenediaminetetraacetate.

The ^{60}Co was obtained by irradiation of cobalt carbonate in the IEA–R1 swimming pool reactor with a thermal neutron flux of 10^{12} n · cm^{-2} · s^{-1} for about 40 hrs.

Solutions of 0.5 g/ml ammonium citrate, 0.10 g/ml potassium cyanide and 0.20 g/ml hydroxylamine hydrochloride, used for elimination of interfering elements were purified by eliminating any lead ions that might be present in them, by extracting the lead ions with a dithizone solution, in accordance with SANDELL.[4]

Preparation of the radioreagent solution. This solution was prepared by adding calculated amounts of EDTA solution to a labelled ^{60}Co solution containing $NaClO_4$. Final concentration of the electrolyte $NaClO_4$ was equal to 0.10M. The pH of the solution was adjusted to 4.6 since at this pH a maximum yield for the displacement of lead was obtained. The labelled Co-EDTA concentration varied from $5.0 \cdot 10^{-3}$ M to $1.0 \cdot 10^{-2}$ M. The specific activity of these solutions ranged from $1.0 \cdot 10^{8}$ cpm/M to $1.0 \cdot 10^{9}$ cpm/M.

To avoid the reaction of lead with any unreacted EDTA, preventing in this way the displacement of cobalt from the Co-EDTA complex, the quantity of cobalt added for preparing the radioreagent solution was always in excess as compared to the EDTA quantity. The contribution due to this slight excess of cobalt was eliminated by carrying out a blank determination for each lead analysis.

The radioreagent solution was stored in polyethylene containers and its concentration did not change during at least six months after its preparation, presenting the same value for blank activity.

Preparation of tetracycline – benzyl alcohol solution. Tetracycline hydrochloride was synthesized and purified by "Laborterãpica Bristol", SP, Brasil.

Tetracycline-benzyl alcohol solution was prepared by equilibrating a 0.020M tetracycline solution in benzyl alcohol with an equal volume of an aqueous phase of 0.10M sodium perchlorate at a pH value of 4.6. Final concentration of TC in the benzyl alcohol phase was determined by analyzing dilute aliquots of the aqueous phase, by spectrophotometry, and subtracting the aqueous concentration value from 0.020M. The final concentration of TC in the benzyl alcohol solution turned out to be equal to $1.67 \cdot 10^{-2}$ M.

The pH of the radioreagent solution was kept equal to 4.6. In this way when the tetracycline-benzyl alcohol solution was added to it no adjustment of pH was required.

Preliminary experiments

The purpose of the preliminary experiments was to establish the experimental conditions for the development of the analytical method.

Study of possible extraction of cobalt ions and Co-EDTA into pure benzyl alcohol. Results presented in Table 1 show that Co^{2+} and Co-EDTA are not

Table 1
Extraction of cobalt ions and Co-EDTA complex into benzyl alcohol

Co^{2+}		Co-EDTA	
pH	E,* %	pH	E, %
2.50	0.4	2.60	0.2
3.10	0.5	2.85	0.3
3.20	0.3	3.20	0.2
3.55	0.3	3.75	0.2
3.95	0.5	4.05	0.2
4.15	0.6	4.40	0.1
4.25	0.3	4.65	0.1
4.55	0.4	4.90	0.1
5.35	0.8		

*E: percentage extraction. Experimental conditions: [Co] = $1.8 \cdot 10^{-5}$ M; [Co-EDTA] = $1.0 \cdot 10^{-2}$ M; [$NaClO_4$] = 0.10M; shaking time: 5 min

extracted into pure benzyl alcohol, indicating that this diluent may be used for the cobalt-tetracycline complex extraction.

Extraction of cobalt with tetracycline – benzyl alcohol solution. The optimum pH for quantitative extraction of cobalt into tetracycline – benzyl alcohol solution was investigated and the results are shown in Fig. 1. The cobalt extraction was

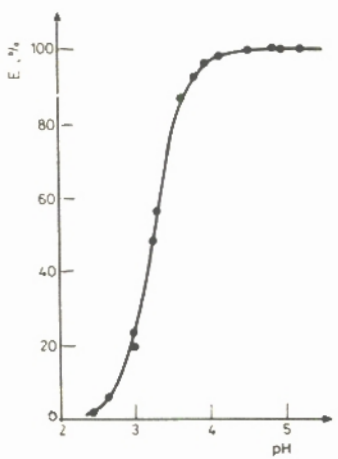

Fig. 1. Extraction percentage (E) of Co-TC complex as function of pH. [Co] = $1.8 \cdot 10^{-5}$ M; *[$NaClO_4$] = 0.10 M; [Tetracycline] = $1.67 \cdot 10^{-2}$ M; shaking time: 5 min; temperature: 25 °C*

complete from a pH value of 4.0 and up. Extraction equilibrium is attained rather rapidly, the corresponding time being less than 5 min.

Effect of pH of the displacement reaction on reaction yield. The results concerning the reaction yield as a function of the pH of the displacement reaction are presented in Table 2. It can be seen that the yield is maximum at a pH value of 4.6.

Table 2
Reaction yield (η) for lead as function of the pH of the displacement reaction

pH	η, %
2.50	95.0
2.70	94.8
3.15	95.3
3.75	96.2
4.25	96.6
4.50	98.9
4.60	99.4
4.70	98.3
5.10	98.2
5.20	87.0
7.75	86.5

[Pb] = 20.72 μg/ml; [Co*-EDTA] = $1.0 \cdot 10^{-2}$ M
Specific activity of the radioreagent: $1.1 \cdot 10^{6}$ cpm/M. Shaking time for displacement reaction: 5 min. Shaking time for extraction: 5 min

Effect of shaking time and of concentration of radioreagent on the displacement reaction. This study was made with 10.36 μg of lead, using a mechanical stirrer.

For $5.0 \cdot 10^{-3}$ M and $1.0 \cdot 10^{-2}$ M radioreagent solutions it was verified that equilibrium was attained rather rapidly. About 5 min of shaking is enough in order to obtain a practically complete displacement of cobalt by lead (reaction 1). By using a radioreagent solution with a lower concentration ($1.0 \cdot 10^{-3}$ M), the reaction yield was only 70%, even after 30 min of shaking. For this reason concentration of the radioreagent was never smaller than $5 \cdot 10^{-3}$ M.

Interference studies

Elements whose formation constants for the EDTA chelate are larger than that of cobalt ions will displace cobalt from the labelled chelate, giving higher values for ^{60}Co activity and false results for lead analysis.

Table 3
Interference of elements

Element	Mass of Pb determined, μg*	Result***
No interferer	10.1 ± 0.8**	–
51.8 μg Ba^{2+}	10.9	N
52.0 μg Sr^{2+}	10.3	N
51.8 μg Mg^{2+}	9.9	N
52.0 μg Ca^{2+}	9.8	N
51.8 μg Mn^{2+}	41.8	Y
103.6 μg La^{3+}	11.1	N
103.6 μg Al^{3+}	57.6	Y
52.2 μg Cd^{2+}	27.1	Y
51.8 μg Zn^{2+}	42.5	Y
158.8 μg V^{5+}	67.4	Y
58.9 μg Ni^{2+}	18.0	Y
51.6 μg Cu^{2+}	39.8	Y
104.1 μg Yb^{3+}	32.0	Y
51.7 μg Hg^{2+}	10.7	N
54.1 μg Th^{4+}	16.2	Y
51.8 μg Cr^{3+}	10.7	N
51.5 μg Fe^{3+}	44.3	Y
104.2 μg Sc^{3+}	70.8	Y

*Mass of lead added: 10.36 μg.
**Mean of seven determinations.
***Y – indicates interference, N – indicates no interference. Specific activity of the radioreagent: $2.4 \cdot 10^8$ cpm/M; pH 4.6; shaking time: 5 min for displacement reaction and 5 min extraction.

To be considered an interfering element, the result of lead analysis carried out in the presence of this element must fall outside the interval m ± 2s (m is the result of lead analysis carried out without the interfering ion and s is the standard deviation). Table 3 presents the interference due to the elements Th^{4+}, Sc^{3+}, Yb^{3+}, Cu^{2+}, Ni^{2+}, V^{5+}, Zn^{2+}, Cd^{2+}, Al^{3+}, Mn^{2+} and Fe^{3+} in the determination of lead.

Table 4
Results of lead determination by the radioreagent method applied after previous separation of Pb ions with dithizone

Interfering elements	Mass of Pb determined, μg*
No interferer	48.0 ± 3.0**
61 μg Co^{2+}	49.5
608 μg Co^{2+}	46.5
52 μg Zn^{2+}	54.0
518 μg Zn^{2+}	46.5
52 μg Cu^{2+}	47.5
518 μg Cu^{2+}	46.5
52 μg Mn^{2+}	46.0
518 μg Mn^{2+}	46.5
52 μg Fe^{3+}	53.5
518 μg Fe^{3+}	48.5
52 μg Al^{3+}	44.0
52 μg Ni^{2+}	52.5
516 μg Ni^{2+}	47.0
44 μg V^{5+} + 59 μg Th^{4+} + 52 μg Sc^{3+} + + 52 μg Yb^{3+} + 52 μg La^{3+}	45.0
52 μg Cd^{2+}	50.0
104 μg Cd^{2+}	51.0
261 μg Cd^{2+}	148.5
522 μg Cd^{2+}	219.5
49 μg Sn^{4+}	34.0
49 μg Sn^{4+} + (Masking agent: 5 g of K Na tartrate)	50.5
60 mg Ca^{2+} + 8 mg Mg^{2+} + 2 mg PO_4^{3-}	0

*Mass of lead added: 51.8 μg.
**Mean of five determinations.

The study of the application of the radioreagent method using artificial samples containing interfering elements was carried out making a previous chemical separation of lead from the interfering ions by the dithizone method.[4] This method consists in the quantitative extraction of lead from a basic solution containing ammonium citrate and potassium cyanide. Results are presented in Table 4.

In the case of cadmium ions, results of Table 4 show that complete elimination of cadmium interference depends on the concentration of cadmium in the sample. If cadmium ions are still present after separation with dithizone, its interference may be eliminated using sodium diethyldithiocarbamate (DDC) as masking agent for the cadmium – EDTA reaction. In the case of determination of 51.8 μg of

lead a mass of 500 μg of DDC was suitable for masking 26.1 μg of Cd remaining after separation with dithizone.

If tin is present, it is converted into metastannic acid that will be the cause of loss of lead by occlusion. Interference of tin may be eliminated by the dithizone pre-separation procedure, using a 0.50 g/ml sodium potassium tartrate solution, instead of ammonium citrate.

In the presence of large amounts of calcium, magnesium and phosphorus, the dithizone extraction procedure fails. The phosphates of these metals are insoluble and they occlude lead hindering quantitative extraction of lead. However, these elements may be removed by using an anionic resin according to the method presented by JOHNSON and POLHILL.[7] Lead and the interfering elements, present in a 1N HCl solution, were passed into a column of the anion-exchange resin in the chloride form. Lead retained in the resin was recovered by elution with 0.01N HCl. If bismuth is present, after the dithizone extraction procedure, it may be eliminated by extraction with successive portions of dithizone, at pH value of 2.0, until the last portion does not show an orange colour.

Treatment of samples

Dissolution of solid samples. Solid samples (aerosols collected on Millipore filters, simulated-air filters, dried animal whole blood and calcined animal bone) were transferred to a beaker and 10 to 25 ml of concentrated nitric acid were added. The beaker was covered with a watchglass and gently heated to boiling until the contents were nearly dry. After that 2 to 10 ml of a 1:1 HNO_3 solution and 2 to 10 ml of a 70% $HClO_4$ were added and the solution was heated to boiling. At this point the solution is practically colourless. The solution was evaporated to dryness and the residue taken up in dilute hydrochloric acid, with gentle heating. For blood and bone samples filtration was necessary in order to a clear the solution after acid digestion. No loss of lead occurred in this filtration, which was checked by analyzing samples with known content of lead.

Treatment for water and gasoline samples. For fresh water samples, the sample was transferred to a beaker and the solution was evaporated to dryness. The residue was taken up in dilute hydrochloric acid.

For gasoline sample, lead should first be transferred into an aqueous phase by diluting 25 ml of gasoline with petroleum ether and then equilibrated with 10 ml of a solution containing 1M ICl, 5M HCl and 6.9% KIO_3.

Previous separation of interfering elements

The sample solution (10–20 ml) was placed in a separatory funnel containing 10 ml of ammonium citrate and 1 ml of hydroxylamine hydrochloride solution. The pH of the solution was adjusted to nearly 9.3 by using NH_4OH solution and then 4 ml of KCN solution was added. Lead extraction was made with 10 ml of $5.0 \cdot 10^{-4}$ M dithizone-carbon tetrachloride solution, for 2 min.

In order to obtain complete extraction of lead, the extraction was repeated with another 10 ml portion of the dithizone – carbon tetrachloride solution.

The lead in the organic phase was back-extracted into an aqueous phase with two portions of 5 ml of 1:100 nitric acid solution. The aqueous solution was evaporated until dryness and the residue was taken up with water.

Radioreagent procedure

The sample solution was transferred to a separatory funnel containing 5 ml of radioreagent. The funnel was shaken mechanically for 5 min in order to allow a complete displacement reaction between Pb and Co*-EDTA.

The cobalt released and the excess of cobalt present in the aqueous solution were then extracted into 5 ml of tetracycline-benzyl alcohol solution by mechanically shaking the funnel for 5 min. The aqueous phase was discarded. Complete separation of the organic phase was made by centrifugation and the radioactivity of an aliquot of this organic extract was measured using a single channel gamma-ray spectrometer coupled to NaI(Tl) well-type scintillation detector.

A blank was analyzed in the same experimental conditions including the operation of sample dissolution and using the same volumes of reagents as used for actual samples.

The activity of the cobalt released in the actual sample was then determined by subtracting the activity due to ^{60}Co found in the blank. This activity value gives the mass of lead in the sample by using calibration graphs such as the ones in Fig. 2.

Results

Verification of a linear relationship between concentration of lead and activity of released cobalt

Two curves were obtained. One using a standard solution of lead nitrate and other using an aerosol sample solution with known lead content. For the aerosol sample, separation of interfering elements with the dithizone procedure was

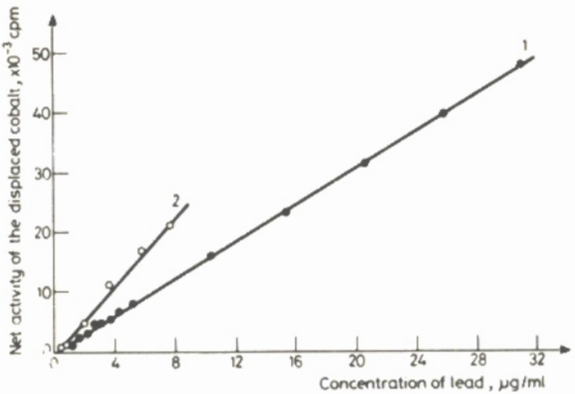

Fig. 2. Net activity of the displaced cobalt (y) as function of concentration of lead (x); $y = a_i x + b_i$. Curve 1 – Standard lead nitrate solution. Specific activity of radioreagent: $3.4 \cdot 10^8$ cpm/M. $a_1 = 1534.76 \pm 8.43$; $b_1 = 103.48 \pm 112.56$; c_1 = (correlation coefficient) = 0.9998. Curve 2 – Aerosol sample solution. Specific activity of radioreagent: $6.6 \cdot 10^8$ cpm/M. $a_2 = 2968.54 \pm 103.72$; $b_2 = -896.114 \pm 414.048$; $c_2 = 0.9970$

Table 5
Verification of non-systematic errors

Sample 1		Sample 2	
Pb found (Y), µg	Pb added (X), µg	Pb found (Y), µg	Pb added (X), µg
2.25	2.60	1.9	2.1
4.11	5.20	3.8	3.6
7.80	7.75	4.8	4.1
9.56	10.35	9.6	8.3
15.40	12.95	19.1	20.1
15.85	15.55	28.7	30.0
17.81	18.15	38.3	37.1
21.25	20.70		
25.65	25.90		
52.40	51.80		
76.05	77.70		
104.15	103.60		
128.45	129.50		
156.40	155.50		

Sample 1 – Standard solution of lead nitrate without interference.
Sample 2 – Aerosol sample solution (with interference) with known lead content.
$Y = a_i X + b_i$
$a_1 = 1.0001 \pm 0.0005$; $b_1 = -0.008 \pm 0.073$; c_1 (correlation coefficient) = 0.9998
$a_2 = 0.999 \pm 0.035$; $b_2 = -0.001 \pm 0.140$; $c_2 = 0.9969$

applied. Fig. 2 shows the results of net radioactivity of cobalt versus concentration of lead.

The least squares method was applied to determine the slopes of the curves, the intercept of the straight lines, their respective standard deviations as well as the correlation coefficients. The values obtained for these parameters are also given in Fig. 2. The values of the correlation coefficients determined were close to one and this indicated a linear correlation between the activity of the cobalt released and the concentration of lead, within the concentration range studied.

Results for the mass of lead found versus mass of lead added is presented in Table 5. Applying the Student t-criterion[8] to these data, it was verified that the slope of the corresponding straight line was estimated, at a confidence level of 0.95, as equal to one and the intercept was estimated as zero, indicating that the method is not subject to systematic errors.

Table 6
Study of precision and accuracy of the method

Mass of lead, μg		
Sample 1	Sample 2	Sample 3
9.7	52.5	49.0
10.1	48.5	44.5
9.1	49.0	49.5
9.8	50.4	48.0
10.3	51.5	46.5
11.9	50.9	45.5
10.0	47.8	46.0
		48.0
		48.0
$\bar{x}$ * = 10.1 ± 0.8**	$\bar{x}$ = 50.0 ± 1.6	$\bar{x}$ = 47.2 ± 1.7
E_{rel} = 7.5%	E_{rel} = 3.2%	E_{rel} = 3.5%
E_p = 2.5%	E_p = 3.5%	E_p = 8.9%

* $\bar{x}$ = mean value
** – standard deviation(s) of a single result
E_{rel} = $(S/\bar{x})$ 100 (relative standard deviation).
E_p = $100(\bar{x}-\mu)/\mu$(relative error).
μ = "true value".
Mass of Pb added: sample 1, 10.31 μg; sample 2, 51.80 μg; sample 3, as sample 2 plus 50 μg of each interfering element: Fe, Al, Mn, Ni, Cd, Zn, Cu, Co, V, Th, Sc, Yb and La.

Precision and accuracy of the method

Reproducibility and accuracy studies were carried out with two samples: a sample without interfering elements and another with interfering elements. For this latter sample a previous lead separation was carried out. Results are presented in Table 6. Relative standard deviations and relative errors for these results have values lower than 10%, indicating that the method is reproducible and accurate.

A result of 91.1 ± 3.2% was obtained as mean value for the yield of the method and this value was used for calculating the lead concentration in aerosol, simulated-air filter and blood samples. For analysis of bone and water the Ca, Mg and PO_4^{3-} interferers were previously eliminated using an anionic resin as described.[7] In this case a yield of 79.9 ± 3.8% (mean of five analyses) was obtained and used for calculating lead in this type of samples.

Limit of detection of the method

In order to estimate the limit of detection of the method, the blank value was determined. Using a radioreagent with specific activity of $1.18 \cdot 10^8$ cpm/M the mean value of the activity for the blank, in four determinations, was equal to 10404 ± 127 cpm, including the background. If we consider the limit of detection as being equal to three times the standard deviation in the blank activity, the limit of the detection for the method, calculated with calibration graphs, will be equal to 0.7 μg of lead.

In the case of the existence of interfering elements, which have to be separated as has been shown, and using a radioreagent with specific activity equal to $5.6 \cdot 10^8$ cpm/M, the mean value of the activity of the blank in eight determinations, was equal to 96725 ± 2333 cpm including the background. The corresponding limit of the detection was equal to 2.6 μg.

Applications

Analysis of filter papers. Two types of filter papers were analyzed: Millipore Filter used for suction of air and the same type of filter paper of which the IAEA samples of simulated-air filters were made of. In none of them was lead found by the radioreagent method.

Analysis of aerosol samples. Aerosol samples were collected by suction of air through Millipore AA filters in places near a lead melting oven and in places far

Table 7
Results of lead analysis in aerosol samples

Samples*	Pb determined, $\mu g/m^3$ of air
OF–A1	3.1 ± 0.2
OF–A2	2.8 ± 0.1
OF–A3	2.3 ± 0.4
OF–A4	3.7 ± 0.3
OF–B1	3.9 ± 0.1
OF–B2	1.2 ± 0.3
PA–1	0.79 ± 0.03
PA–2	0.78 ± 0.03
PA–3	0.88 ± 0.03
LR–1	0.10 ± 0.01

*Samples OF–A: collected at 1 m from melting oven.
Samples OF–B: collected at 30 cm from oven.
Samples PA : collected in an office.
Sample LR : collected in a radiochemical laboratory.

from the lead oven. Samples were also collected in other working places, such as offices and radiochemical laboratories. The volume of air withdrawn in each filter varied from 25 to 150 m^3. Results are presented in Table 7.

Analysis of samples provided by IAEA. For the analysis of each material the following amounts were used: 5 ml of fresh water (W-3), 2.0 g of calcined animal bone (A-3/1) and 5.0 g of dried animal whole blood (A-2). For aerosol and simulated-air filter samples, the content of the material present in one filter-paper was analyzed.

In Table 8 the results of these analyses are presented. In the case of bone and blood analysis the IAEA recommended values[9] are presented for comparison. For water and simulated-air filter samples only the concentration ranges were available to us.

The relative standard deviations were lower than 11%, which is usually considered as a good result in trace analysis. The study of accuracy was made for bone and blood analysis by comparison of the mean results with the IAEA recommended values. Student's t-test[8] was used for such comparison. By this criterion, with a confidence level of 0.90, the results obtained in this work are equal to the recommended values.

Analysis of gasoline. The radioreagent method was used for analyzing organic lead in gasoline.

Table 8
Lead analysis in samples provided by the IAEA

Sample	Pb results	IAEA recommended values
Blood (A–2)	1.0 ppm 1.0 0.9 1.0 0.9 1.0 ± 0.1	0.972 ± 0.090 ppm
Bone (A–3/1)	5.9 ppm 6.0 5.6 5.5 6.3 5.8 ± 0.4	6.75 ± 1.0 ppm
Simulated-Air Filter (Air-3)	7.1 μg 5.8 6.1 5.5 6.1 ± 0.7	(range: 1–10 μg)
Fresh water – ampoule a (W–3) – ampoule b	16.1 μg 34.6 μg	(range: 5–50 μg)

Table 9
Analysis of lead in gasoline

Leaded gasoline, mg Pb/ml	Natural gasoline, mg Pb/ml
436	57.2
413	56.4
489	48.8
441	61.6
	56.8
445 ± 32	
	56. ± 5

The American Society for Testing Materials (ASTM) method[10] was chosen for previous separation of interferences. This method consists in transferring lead from gasoline into an aqueous phase as described in the part of Treatment of samples, and then to eliminate the interfering ions by the dithizone method. Next the radioreagent method was applied to determine lead. Results are presented in Table 9 and show also good precision for this type of sample.

Discussion

The radioreagent method of analysis presented in this paper complies with the basic requirements for the feasibility of the method,[1] meaning availability of a radioreagent ^{60}Co-EDTA, which reacts with the sought element lead; a suitable radioisotope, ^{60}Co, exists to label the reagent EDTA; the reaction between the sought element and the radioreagent is complete in a rather short time (less than 5 min); the radioactive product, ^{60}Co, is separable from the reagent in excess by a simple solvent extraction separation method; interference from foreign elements in the samples can be eliminated; blank activity can be kept at a reasonably low value.

Precision and accuracy are good for various types of tested samples and the method is not subject to systematic errors.

Sensitivity, expressed as limit of detection, is equal to 2.6 μg and 0.7 μg of lead for a sample with and without interference, respectively, and specific activity for the reagent, as $5.6 \cdot 10^8$ cpm/M and $1.18 \cdot 10^8$ cpm/M in each case.

*

The authors are grateful to Dr. Ney GALVÃO, to Mr. A. A. LARANJA and to "Laborterāpica Bristol", São Paulo, for a generous gift of tetracycline.

References

1. M. P. MENON, J. Radioanal. Chem., 43 (1978) 309.
2. L. G. SILLÉN, A. E. MARTELL, Stability Constants of Metal Ion Complexes, Spec. Publ. 25 (Suppl. 1), The Chemical Society, Burlington House W1V, London, 1971.
3. L. G. SILLÉN, A. E. MARTELL, Stability Constants of Metal-Ion Complexes, Spec. Publ. 17, The Chemical Society, Burlington House W1V, London, 1964.
4. E. B. SANDELL, Colorimetric Determination of Traces of Metals, Interscience Publ. Ltd., New York, 1959, p. 410, 555–583.

5. M. SAIKI, M. J. C. NASTASI, F. W. LIMA, J. Radioanal. Chem., 64 (1981) 83.
6. N. P. SACHAN, C. M. GUPTA, Talanta, 27 (1980) 457.
7. E. I. JOHNSON, R. D. A. POLHILL, Analyst, 82 (1957) 238.
8. V. V. NALIMOV, The Applications of Mathematical Statistics to Chemical Analysis, Pergamon, Oxford, 1963.
9. L. GORSKI, J. HEINONEN, O. SUSCHNY, IAEA Rept. (IAEA/RL/25), Vienna, 1974.
10. American Society for Testing and Materials. Standard test method for trace amounts of lead in gasoline. Oct. 1972 (ASTM-D-3116-72). In: 1980 Annual book of ASTM Standards—Part 25: Petroleum products and lubricants (III): D-2981-latest; aerospace materials; catalysts p.33 7.