## A Radiochemical Method for Selective Determination of Traces of Lead

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# A Radiochemical Method for Selective Determination of Traces of Lead

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A very simple and rapid radiochemical method for the determination of 0.01—1 mcg of lead has been developed. It consists of adding carrier-free $^{212}Pb$ to the analysed sample, followed by shaking with a standard lead diethyldithiocarbamate solution in carbon tetrachloride. The amount of non-active lead in the sample is determined from activities of the organic and aqueous phases. A 10-fold excess of bismuth and more than 50-100-fold excess of other metals extractable as diethyldithiocarbamates do not interfere in the determination.

## INTRODUCTION

Traces of lead are usually determined by solvent extraction with dithizone, using potassium cyanide as masking agent;[1,2] however, thallium(I) and bismuth in equal amounts and iron(III) in greater excess seriously interfere and have to be removed. Moreover, the dithizone method, as well as other analytical methods, requires the quantitative isolation of lead from the sample, which is in many cases rather difficult. This difficulty can be avoided by using carrier-free $^{212}Pb$, as the separation yield can be determined easily from the radioactivity measurements.

The aim of the present paper was to develop a simple, rapid, selective and sensitive radioanalytical method for the determination of traces of lead.

Neutron-activation analysis is not suitable for this purpose because of its low sensitivity. Substoichiometric determination of lead with dithizone is selective but not very sensitive[3] due to the low value of the extraction constant $K_{ex}$ (log $K_{ex}$ = 1.0 for carbon tetrachloride as organic solvent).[4] The extraction of lead diethyldithiocarbamate into carbon tetrachloride is much more suitable in this respect because of the high stability of this chelate (log $K_{ex}$ = 8.0).[4] Unfortunately, our preliminary experiments showed that the extraction of lead with a substoichiometric amount of zinc diethyldithiocarbamate (this reagent is more stable than diethyldithiocarbamic acid itself) is rather slow. During these experiments it was found that the two-phase isotope exchange between lead diethyldithiocarbamate in the organic phase and lead tartrate in the aqueous phase is rapid even for very low concentrations of lead and this fact has been utilized in the development of the present method. It is of interest to note that the two-phase isotope exchange between bismuth diethyldithiocarbamate and bismuth tartrate complex in similar conditions is extremely slow.[5]

## THEORETICAL

The principle of the present method consists of adding carrier-free $^{212}$Pb to the analysed sample containing an unknown amount ($x$) of lead. Then ammonium tartrate is added and the solution is shaken with standard lead diethyldithiocarbamate in carbon tetrachloride containing a known amount ($m$) of lead. After the isotope equilibrium is reached the specific activities of lead are distributed in the aqueous and organic phases according to the following equation:

$$\frac{A_{aq}}{x} = \frac{A_{org}}{m} \qquad (1)$$

$A_{aq}$ and $A_{org}$ denote the measured activities of lead in the aqueous and organic phases, respectively.

The practical application of the two-phase isotope exchange in trace analysis requires a high stability of the chelate in the organic phase in the absence of the excess of organic reagent even at highest dilutions. The optimum conditions for the determination can be predicted from the theory of substoichiometry:[6]

$$pH > -0.01 \log c_{PbA_2} - \tfrac{1}{2}\log K_{ex} + \tfrac{1}{2}\log (1 + \beta_1[Tart^{2-}]) \qquad (2)$$

where $c_{PbA_2}$ is the concentration of lead diethyldithiocarbamate, $\beta_1$ is the stability constant of lead tartrate (log $\beta_1$ = 2.9)[2], and [Tart$^{2-}$] is the equilibrium concentration of tartrate anion. For the determination of submicrogram amounts of lead the value of $c_{PbA_2}$ has to be of the order of $10^{-6}$ —

$10^{-7}$ M. From Eq. (2) it is evident that pH has to be higher than 6 when $[\text{Tart}^{2-}] = 0.2$ M.

The extraction of lead as diethyldithiocarbamate in the presence of potassium cyanide is rather selective; only thallium(I), thallium(III), bismuth and partially also indium and antimony(III) are extracted simultaneously with lead.[2] In the two-phase isotope exchange reaction, thallium(I), indium and antimony(III) will not interfere, because their extraction constants are much lower than those of lead.[2,4] The interference of bismuth and thallium(III) can be substantially decreased by the presence of tartrate which forms much more stable complexes with these metals than with lead.[2]

## EXPERIMENTAL

### Apparatus and equipment

A pH-meter (Radiometer TTT-1, Copenhagen) with glass electrode and a scintillation counter with the well-type NaI(Tl) crystal (channel 0.238 MeV) were used. Reactions were carried out in 20-ml glass test tubes with ground-glass stoppers.

### Reagents

Unless otherwise stated, all reagents, including sodium diethyldithiocarbamate, were of analytical-reagent-grade purity. Carbon tetrachloride was distilled twice. The preparation of the buffer solutions was as follows. Buffer solution A. Dissolve 11.5 g of sodium tartrate and 3.3 g of potassium cyanide in 50 ml of water. Adjust pH with sodium hydroxide to about 12. Buffer solution B. Dissolve 9.2 g of ammonium tartrate and 3.3 g of potassium cyanide in 50 ml of water (pH about 9.5).

To prepare the standard lead diethyldithiocarbamate solution add to 20 ml of aqueous lead nitrate solution (pH 2–6), containing 20.0 or 2.0 mcg of lead, 5 ml of buffer solution A, 60 ml of carbon tetrachloride, and 1–2 mg of solid sodium diethyldithiocarbamate. Shake for 2 min and separate carefully the organic extract containing 1.0 or 0.1 mcg Pb/3 ml. Thus prepared, the solution contains less than $10^{-9}$ M free diethyldithiocarbamic acid. Carrier-free $^{212}$Pb is prepared from RdTh ($^{228}$Th, T = 1.91 y) solution (pH ∼ 2) which is in the radioactive equilibrium with the daughter nuclides $^{224}$Ra (T = 3.64 day), $^{220}$Rn (T = 51.5 sec), $^{216}$Po (0.158 sec), $^{212}$Pb (10.5 hr), $^{212}$Bi (60.5 min), $^{208}$Tl (3.1 min) and $^{212}$Po ($3 \times 10^{-6}$ sec). To 2.5 ml of the RdTh solution in a glass test tube 0.5 ml of buffer A, 6 ml of carbon tetrachloride and about 0.1 mg of solid sodium diethyldithiocarbamate are added. Shake for 2 min, transfer the organic extract into another

test tube and reextract $^{212}$Pb into 2 ml of 1 M hydrochloric acid (2 min shaking). Separate the aqueous phase and dilute 20 times with water (activity about $10^5$ cpm/ml).
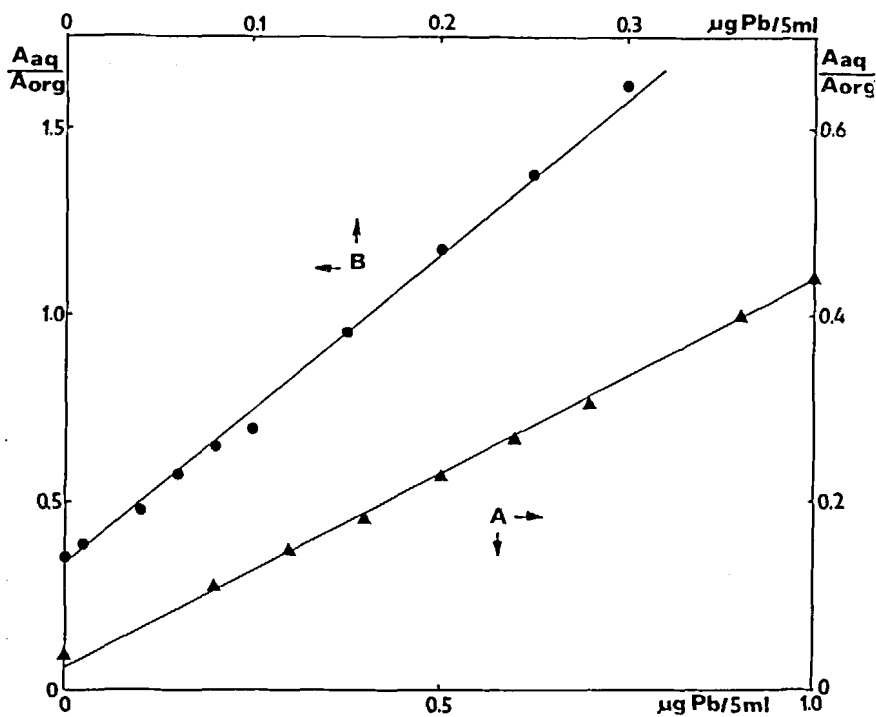


FIGURE 1   Calibration curve for the determination of lead. The amount of lead in standard lead diethyldithiocarbamate solution is 1.0 mcg (Curve A) and 0.1 mcg (Curve B).

## Two-phase isotope exchange

The time necessary for attaining complete isotopic exchange between lead tartrate and lead diethyldithiocarbamate was studied radiometrically, labelling alternately the first or the second complex with $^{212}$Pb. It was found that at pH 9.5 the equilibrium was reached in 1–2 min in the concentration range studied. In the absence of tartrate or at lower pH-value the kinetics of the isotopic exchange is substantially slower.

## Procedure

To 5.0 ml of an analysed sample (pH 2–6), labelled with carrier-free $^{212}$Pb, add 1.0 ml of buffer B (final pH~9.5) and shake for 2–4 min with 3.0 ml of

standard lead diethyldithiocarbamate solution in carbon tetrachloride. Measure the activity of 2.0-ml aliquots of the organic and aqueous phases immediately (channel 0.238 MeV) or after 5 hr (after reaching the radioactive equilibrium between $^{212}Pb$ and $^{212}Bi$).

## Influence of foreign ions

The possible interference of a great number of metals in the determination of lead by the above method was studied in the following way: samples containing 1.00 mcg of lead and 10–100 mcg of other metals were analysed for the lead content as described in Procedure.

### TABLE I

Determination of lead in the presence of foreign metals

| Lead present (mcg) | Foreign metals present (mcg) | Lead found (mcg) | Difference (%) |
|---|---|---|---|
| 1.00 | $V^V(50)$ | 1.03 | +3 |
| 1.00 | $Cr^{III}(50)$ | 1.05 | +5 |
| 1.00 | $Mo^{VI}(50)$ | 0.96 | −4 |
| 1.00 | $W^{VI}(50)$ | 0.95 | −5 |
| 1.00 | $Mn^{II}(100) \, Co^{II}(100) \, Ni(100)$ | 1.00 | 0 |
| 1.00 | $Fe^{III}(100)$ | 1.05 | +5 |
| 1.00 | $Pd(100)$ | 1.02 | +2 |
| 1.00 | $Cu(100) \, Ag(100) \, Au^{III}(100)$ | 1.03 | +3 |
| 1.00 | $Zn(100) \, Cd(100) \, Hg(100)$ | 1.00 | 0 |
| 1.00 | $Ga(50)$ | 1.06 | +6 |
| 1.00 | $In(100)$ | 0.95 | −5 |
| 1.00 | $Tl^I(100)$ | 1.03 | +3 |
| 1.00 | $Tl^{III}(10)$ | 0.99 | −1 |
| 1.00 | $Ge(100) \, Sn^{II}(100)$ | 1.04 | +4 |
| 1.00 | $As^{III}(100) \, Sb^{III}(100)$ | 0.93 | −7 |
| 1.00 | $Bi(10)$ | 1.06 | +6 |
| 1.00 | $Se^{IV}(100)$ | 0.95 | −5 |
| 1.00 | $Te^{IV}(10)$ | 1.02 | +2 |

## RESULTS AND DISCUSSION

A number of samples with various known amounts of lead were analysed by the procedure described above. The amount of lead in standard lead diethyl-dithiocarbamate solution was 1.0 mcg/3 ml for the determination of 0.1–1.0 mcg of lead and 0.1 mcg/3 ml for the determination of 0.01–0.1 mcg of lead. The values of the ratio $A_{aq}/A_{org}$ were plotted against $x$ (cf.

Figure 1, curves A, B). The length of abscissa at the intersection is given by the blank experiment. The practical applicability of the method was tested by determining lead in the presence of a number of metals extractable as diethyl-dithiocarbamate. The results are summarized in Table I. From other elements only bismuth present in more than 10-fold excess interferes. Other elements do not interfere when present in 50–100-fold excess. The selectivity can be further increased by the preliminary separation of lead which need not be quantitative. The separation yield can be determined easily from the initial and final activity.

The proposed method is very simple, rapid, and selective. Because of the short half-life of $^{212}Pb$ (10.5 hr) the method is free from health hazards or laboratory contamination danger. Both the sensitivity and selectivity are much higher than those of the dithizone method.

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