

## RADIOMETRIC TRACE ANALYSIS OF LEAD WITH DIETHYLDITHIOCARBAMATE AND $^{204}\text{Tl}^*$

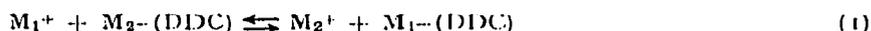
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(Received March 30th, 1961)

### INTRODUCTION

Preliminary radiometric experiments<sup>1</sup> on trace analysis of metals led to the choice of the system:



in which  $\text{M}_1$  is the metal to be determined,  $\text{M}_2$  is a radio-active metal and DDC stands for diethyldithiocarbamate. As the ions are soluble in water, and the DDC-complexes in a solvent which is immiscible with water, separations can easily be effected. Selectivity can be obtained by a proper choice of  $\text{M}_2$ , the pH and masking agents.

The sequence of affinities of metals for DDC was elaborated by WICKBOLD<sup>2</sup>, BODE AND TUSCHE<sup>3</sup> and ECKERT<sup>4</sup>, and used in analysis by SEDIVEC AND VASAK<sup>5</sup>, PRIBIL<sup>6</sup>, MARTENS AND GITHENS<sup>7</sup>, KOVARIK AND VINS<sup>8</sup> and DESZÖ AND FÜLÖP<sup>9</sup>. Spectrophotometry was the basis of all quantitative evaluations.

In our work radio-isotopes are used for this purpose. Selectivity for lead is obtained by carrying out the exchange at pH 14 in the presence of excess potassium cyanide. Only the DDC-complexes of bismuth(III), thallium(III), lead(II) and thallium(I) are stable under these conditions, the stability decreasing in this order. Thus with the radio-isotope  $^{204}\text{Tl}$  two determinations of lead are possible, symbolized by both directions of eqn. (1). These two methods are described in parts A and B respectively.

### EXPERIMENTAL METHOD A

#### *Materials and methods*

*Acid  $^{204}\text{Tl}$  solution.* Dilute 2.4 mg (1 mC) of  $^{204}\text{Tl}^+$  with 1 N nitric acid to 10 ml, add 0.5 ml of bromine water, boil for 30 min, cool, dilute with 1 N nitric acid to 100 ml, and standardise iodometrically (SANDELL<sup>10</sup>) after removal of nitrites.

*Alkaline  $^{204}\text{Tl}$  solution.* Neutralize 8 ml of the above acid solution with sodium hydroxide, dilute to 25 ml, add potassium cyanide and sodium bicarbonate to give a 0.12% solution of each, and adjust to pH 13 and 30 ml with sodium hydroxide. Prepare daily (to avoid adsorption, etc.).

\* Publication 124<sup>b</sup> of the Research Institute for Animal Husbandry "Schoonoord".

<sup>210</sup>Pb solution. 400 µg of lead and 4 µC <sup>210</sup>Pb (Ra-D in equilibrium with its decay products) per ml of 1 N nitric acid.

*DDC-<sup>35</sup>S*. Dissolve 100 mg (3 mC) of DDC-<sup>35</sup>S dihydrate\* in 10 ml of 0.01 N sodium tartrate (AnalaR), add 300 mg of β-mercaptoethylamine hydrochloride and adjust to pH 11 with hydroxide. Store (under nitrogen) in a polyethylene vessel at 4°.

*Ion-exchange water*: resistivity at least 3 Megohms.

*Cyanide-DDC solution (a)*. To 100 ml of 10% potassium cyanide in water, add 0.2 mole of sodium hydroxide and 20 mg of DDC dihydrate (all Merck p.a.\*\*), purify with five 10-ml portions of carbon tetrachloride, store (in polyethylene at 4°) over carbon tetrachloride and purify occasionally by shaking (200 µg DDC/ml).

*Cyanide-DDC solution (b)*. To 100 ml of 1% potassium cyanide in water, add 0.01 mole of sodium tartrate and 0.2 mg of DDC dihydrate. (pH 10.5). Purify and store as (a).

*Cyanide-bicarbonate solution (a)*. 0.1% potassium cyanide containing sodium bicarbonate to give pH 10.

*Cyanide-bicarbonate solution (b)*. Solution (a) adjusted to pH 13 with sodium hydroxide.

*Tartrate*. 0.1 M ammonium tartrate (AnalaR) in water.

*Acid Tl-carrier*. 1 mg Tl(NO<sub>3</sub>)<sub>3</sub> per ml of 2 N nitric acid.

*Tl-(DDC)<sub>3</sub>-carrier*. 0.5 mg Tl as Tl(DDC)<sub>3</sub> per ml of carbon tetrachloride.

The hydrochloric acid (s.g. 1.18), nitric acid (s.g. 1.42), ammonia (s.g. 0.88), chloroform and carbon tetrachloride used were "AnalaR". The radionuclides involved are shown in Table I.

TABLE I

Nuclides	Half-life	β-radiation (MeV)	γ-radiation (MeV)	Measurements <sup>a</sup>	Remarks
<sup>204</sup> Tl	3.9 years	0.76	—	1 <sup>b</sup> ; 2	
<sup>210</sup> Pb <sup>c</sup>	20.4 years	0.018; 0.056	0.047	1	Ra - D
<sup>210</sup> Bi	5 days	1.17	—	1 <sup>b</sup> ; 2	Ra - E
<sup>210</sup> Po	139 days	—	0.79	1	(5.3 MeV-α) Ra - F
<sup>35</sup> S	87 days	0.15	—	3	

<sup>a</sup> *Measurement 1*: A Philips well-type scintillation crystal for 1-ml samples (PW 4111/W) was combined with a scaler PW 4022-32-52 and a E.K.A.F. single channel analyzer. *Measurement 2*: A 20th-Century Electronics M6-GM tube for 10-ml samples, was desiccated between the electrodes to prevent leakage and combined with the Philips scaler. *Measurement 3*: A Philips end-window GM-tube (18506; window thickness 2 mg/cm<sup>2</sup>) was combined with the Philips scaler.

<sup>b</sup> Bremsstrahlung

<sup>c</sup> For the separation of <sup>210</sup>Pb from its decay-products, see below.

The extraction was carried out in a polyethylene pill-case (76 mm high; outer diameter 25 mm), covered with an efficient lid. Shaking was performed (in a vertical position) with a "Microid Flask Shaker" (Griffin and Tatlock) which made a vertical movement of about 0.5 cm. The arm of the shaker was connected to a

\* From the Radiochemical Centre, Amersham (Great Britain).

\*\* Potassium cyanide from Merck contains less than 10 p.p.m. Pb.

simple device for measuring its velocity. A ball-bearing was added to the spindle of the driving motor to give it a more constant velocity for a given position of the dial. To prevent spillage of a radio-active solution in case of an accident, the shaker was placed in a shallow polyethylene trough.

#### *Scheme of method A*

Lead diethyldithiocarbamate is extracted (with carbon tetrachloride) from an alkaline solution (pH 14), containing excess DDC, cyanide (to obtain selectivity) and tartrate (to prevent the precipitation of hydroxides and carbonates). The lead is then exchanged with  $^{204}\text{Tl}^{+3}$ -ions. After an alkaline rinsing to remove residual traces of the aqueous layer, the  $^{204}\text{Tl}$ -activity in the organic layer is measured.

Part of the DDC is coextracted and would react with the  $^{204}\text{Tl}$  during the exchange procedure. As a large excess of DDC is required for the complete extraction of traces of lead, this coextraction of DDC would result in a considerable blank. Thus back-extractions of DDC are inserted.

#### *Selective extraction of lead*

3 ml of an alkaline solution (pH 14), containing 0.1 to 3.0  $\mu\text{g}$  of labelled lead\*, 5% potassium cyanide, 0.01 M tartrate and 300  $\mu\text{g}$  of DDC, were shaken with 8 ml of carbon tetrachloride in the pill-case for 5 min. (A velocity of 800 to 1000 periods per min was optimal: insufficient extraction was obtained at lower velocities and emulsions occurred at higher ones). The pill-case was then centrifuged lightly to ensure complete separation of the phases.

Chloroform was slightly more efficient than carbon tetrachloride but the coextraction of DDC (see below) was also enhanced. The comparatively large volume of the tetrachloride used resulted in a high coextraction of DDC. Comparison of the extractions of lead and DDC, with large volumes of carbon tetrachloride or small volumes of chloroform showed the former method to be superior\*\*.

96% of the lead was extracted (st. dev. 3%). With the exception of bismuth and thallium other metals were not coextracted in appreciable amounts.

*Traces of metals which might be coextracted are back-extracted by cyanide together with the DDC.* Large amounts of iron and copper prevent the extraction of the lead; other ions including mercury(II) and silver(I) are not active in this way. No explanation for this behaviour of iron and copper could be found.

For small amounts of bismuth and thallium a "blank" can be determined by carrying out the extraction with DDC (with part of the sample) in the presence of cyanide and EDTA: lead is not extracted in contrast to bismuth and thallium (KINNUNEN AND WENNERSTRAND<sup>11</sup>).

The extraction of lead is slightly influenced by phosphate and pyrophosphate: up to 100  $\mu\text{g}$  of the latter and 10  $\mu\text{g}$  of the former anion do not interfere in the determination of 0.1  $\mu\text{g}$  of lead; when larger amounts are present citrate has to be added to the acid sample solution as described by SANDELL<sup>10</sup> for the extraction of lead with dithizone.

\* Not separated from its decay-products. Measurement (2) applied and checked after 5 days ( $\tau_{1/2}$  of  $^{210}\text{Bi}$ ).

\*\* A mixture of 6 ml of tetrachloride and 2 ml of chloroform can be used alternatively when the efficiency of the shaker might go down.

*Part of the DDC was coextracted.* In the literature only very approximate values are found for this extraction. BODE<sup>12</sup> (using the colour reaction with excess aqueous copper for detection) stated that the extraction of DDC is negligible above pH 8.5, provided that the carbon tetrachloride is dried by filtration.

In our experiments DDC-<sup>35</sup>S was used to determine the extracted %. As this DDC-<sup>35</sup>S contained small amounts of decomposition products (some of which were more soluble in carbon tetrachloride than the DDC-<sup>35</sup>S itself) the solution was back-extracted three or four times. The organic layer was then pipetted on an aluminium dish, dried and measured. The form of the dish promoted a homogeneous distribution and thus minimized the error due to a variable selfadsorption (Fig. 1\*).

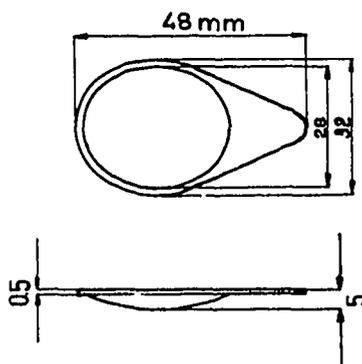


Fig. 1. Aluminium tray.

From 0.2 to 0.4% of the <sup>35</sup>S was found in the organic layer. Centrifugation up to 2000 rev/min. (Ø 25 cm) was unsuccessful in lowering this blank\*\*. Filtration decreased the "extracted" percentage to about 0.02 but also removed appreciable amounts of lead when applied to a Pb(DDC)<sub>2</sub> solution\*\*\*. Thus the tetrachloride layer contains a DDC surplus of 0.2 to 0.4% (corresponding to a blank of 0.3 to 0.6 µg of lead).

A second DDC surplus results from the incomplete removal of the aqueous layer. Provided that this DDC (1 to 2%) is totally extracted with <sup>204</sup>Tl<sup>+3</sup> during the exchange-procedure, it is equivalent to a blank of 1.5 to 3.0 µg of lead.

#### *Back-extraction of DDC*

As was to be expected from the figures of BODE<sup>12</sup>, strongly alkaline solutions were the most effective, but appreciable amounts of lead were also back-extracted. A solution of pH 10.5 (containing 1% potassium cyanide to prevent the interference of foreign metals) was found to be optimal: 90 to 95% of the DDC and only 1 to 6% of the lead were back-extracted. Again 1 to 2% of the aqueous layer could not be removed. The remaining DDC blank can be calculated to be (theoretically) equivalent to 0.082 µg of lead.

Thus a second back-extraction is required for amounts of lead below 0.5 µg. A

\* With the ordinary dishes - which have a rectangular profile - the last drops of the solvent and thus the precipitate are collected in the outer regions.

\*\* Higher velocities are dangerous with regard to the construction of the pill-case.

\*\*\* Filtration through hydrophobized paper, as recommended by KOVÁCS<sup>13</sup> and WEGMANN<sup>14</sup>, was found to be equally unsatisfactory.

cyanide-DDC solution (resulting from the purification of cyanide with DDC) was used for both strippings instead of cyanide alone. It can be calculated that theoretically the DDC blanks for 1 and 2 back-extractions are enlarged to 115 (st. dev. 60) and 36 (st. dev. 14)  $\mu\text{g}$  of lead respectively by this additional DDC.

It can also be calculated that the whole process is efficient for 87-98 and 81-97% of the lead with 1 and 2 back-extractions respectively. In practice the figures 94 (st. dev. 3) and 89 (st. dev. 7) were found.

#### *Exchange with $^{204}\text{Tl}^{+3}$*

To prevent all interferences from traces of mercury, silver, copper, etc. (present in the reagents and in the pill-case), 0.1% potassium cyanide was added to the alkaline  $^{204}\text{Tl}^{+3}$ -solution used for the exchange with  $\text{Pb}(\text{DDC})_2$ .

A pH of 13 proved to be optimal for a high rate of exchange. With a 3.5-fold excess of  $^{204}\text{Tl}^{+3}$ , the process was effective to 96% (st. dev. 2) within 5 min. Thus the whole procedure was effective to 90% (st. dev. 5) and 85% (st. dev. 9) respectively for the two ranges of lead. For amounts of lead below 0.1  $\mu\text{g}$  the efficiency was only 75% (st. dev. 15).

After the separation of the excess  $^{204}\text{Tl}^{+3}$  from the organic layer, the latter had to be washed in order to remove the usual small traces of the aqueous layer (1 to 2%), as well as part of the  $^{204}\text{Tl}$  "dissolved" in the carbon tetrachloride.

With regard to the aqueous layer traces: after the washing, this factor still resulted in a blank equivalent to 2.2 (st. dev. 1.4) and 0.5 (st. dev. 0.2)  $\mu\text{g}$  of lead for the two amounts of  $^{204}\text{Tl}$  applied in our procedure. With regard to "dissolved"  $^{204}\text{Tl}$ : experiments with ionic  $^{204}\text{Tl}$  and pure carbon tetrachloride indicated a blank of 0.1 to 0.3% (again after the washing)\*. This blank was decreased by filtration but again part of the metal-DDC-complex ( $\text{Tl}(\text{DDC})_3$  here) was adsorbed by the filter paper. This second factor contributes a Tl-blank of 18 (st. dev. 9) and 3.6 (st. dev. 1.8)  $\mu\text{g}$  of lead for the two amounts of  $^{204}\text{Tl}$  used above. This is still small compared with the DDC blank.

#### *Measurement of the radioactivity of $^{204}\text{Tl}$*

$^{204}\text{Tl}$  can be measured in two ways. The sensitivity of both detectors is about equal, but the GM-tube has a lower (and more stable) zero value and is therefore used to measure the small activities. The crystal has the advantage that separate tubes can be used for the samples and thus the detector need not be cleaned between measurements. With both methods  $10^4$  counts are registered resulting in a 1% statistical error.

Direct measurement of the carbon tetrachloride (8 ml) is to be preferred when the GM-tube is used (10 ml capacity). Thallium-DDC carrier is added and the pill-case is thoroughly rinsed to prevent adsorption.

Back-extraction of the  $^{204}\text{Tl}$  from the tetrachloride with a small volume of an acid thallium carrier is to be preferred when the crystal is used (1 ml capacity). (Since a few percent of the excess  $^{204}\text{Tl}^{+3}$  are adsorbed on the walls of the plastic pill-case during the exchange of thallium with lead, this back-extraction has to be carried out in a second container).

\* For chloroform a figure of 0.5 to 0.6% was found.

## PROCEDURE FOR METHOD A

The procedure is given for a sample containing from 0.1 to 0.5  $\mu\text{g}$  of lead and (per  $\mu\text{equiv.}$  of this metal) less than the following amounts of foreign ions (also in  $\mu\text{equiv.}$ ):  $\text{Bi}^{+3}$  0.1,  $\text{Tl}^{+3}$  0.1,  $\text{Fe}^{+3}$  2500,  $\text{Cu}^{+2}$  1500,  $\text{Hg}^{+2}$  10,000,  $\text{Zn}^{+2}$  30,000,  $\text{Ag}^{+}$  10,000,  $\text{PO}_4^{-3}$  300 and  $\text{P}_2\text{O}_7^{-2}$  1000.

Dissolve in nitric and/or hydrochloric acid, evaporate (when necessary) to about 0.5 ml, place in the pill-case, add 0.3 ml of tartrate and neutralize with ammonia to phenolphthalein. The volume should now be about 1.5 ml.

Add 1.5 ml of the cyanide-DDC solution (a) and extract with 8 ml of carbon tetrachloride by shaking for 5 min (800 to 1000 periods per min). Centrifuge for 1 min at 1000 rev./min ( $\varnothing$  25 cm), remove the aqueous layer with a pipet and shake for 2 min with 2 ml of cyanide-DDC solution (b). Repeat this stripping once, centrifuge and remove the upper layer.

Exchange with  $^{204}\text{Tl}^{+3}$  by shaking for 5 min with 0.2 ml of alkaline  $^{204}\text{Tl}^{+3}$  and 0.8 ml of cyanide-bicarbonate solution (b). Centrifuge, remove the aqueous layer, shake for 1 min with 2 ml of cyanide-bicarbonate solution (a), centrifuge and separate.

Add 0.5 ml of the thallium-DDC-carrier, transfer to a calibrated glass tube and rinse the pill-case by shaking twice for 10 min with 0.5 ml of the carrier. Adjust with tetrachloride to 10 ml, pipet into the GM-tube and measure\*.

## RESULTS WITH METHOD A

In Table II the results for the two ranges of lead are shown. To facilitate comparison,

TABLE II  
DETERMINATION OF 0.1 TO 3.0  $\mu\text{g}$  OF LEAD WITH DDC AND  $^{204}\text{Tl}^{+3}$   
(Mean values and standard deviation of 4 experiments each)

1	2	3	4	5	6	7
Lead added ( $\mu\text{g} \cdot 10^{-2}$ )	C/m $^{204}\text{Tl}$ in $\text{CCl}_4$ (minus blank) <sup>a</sup>	Standard deviation	Lead exchanged <sup>b</sup> ( $\mu\text{g} \cdot 10^{-3}$ )	Lead corrected <sup>c</sup> ( $\mu\text{g} \cdot 10^{-3}$ )	Error (%)	Standard deviation (%)
100	770	85	89	10.4	+4	11
200	1540	160	177	208	+4	10
300	2240	250	258	303	+1	11
400	2980	80	343	402	+0.5	3
500	3900	500	450	500	0	13
1000	7950	550	915	1010	+1	7
2000	14800	800	1700	1890	-5.5	5
3000	23000	1700	2650	2930	-2	7

<sup>a</sup> 260 and 1000 C/m for 0.1 to 0.4 and 0.5 to 3.0  $\mu\text{g}$  of lead respectively.

<sup>b</sup> Calculated from column 2; 0.001  $\mu\text{g}$  of  $^{204}\text{Tl}$  in  $\text{CCl}_4$  produces 8.7 C/m in the GM-tube.

<sup>c</sup> As 85 and 90% of the lead are exchanged in the two ranges respectively.

\* With 0.5 to 3.0  $\mu\text{g}$  of lead only one back-extraction is carried out, 1 ml of  $^{204}\text{Tl}(\text{III})$  is used (no cyanide-bicarbonate) and the final organic layer is pipetted into a second pill-case. The first one is rinsed twice for 10 min with 2 ml of the thallium-DDC-carrier and the collected solutions are shaken for 4 min with 0.8 ml of the acid Tl-carrier. After centrifugation the aqueous layer is pipetted into a measuring-tube, the pill-case is rinsed with 0.3 ml of the acid carrier and the collected aqueous solutions are measured with the well-type crystal.

all values are corrected for measurement (of the carbon tetrachloride) with the GM-tube\*.

For the two ranges (0.1 to 0.5 and 0.5 to 3.0  $\mu\text{g}$  of lead) the blanks were found to be equivalent to 30 and 115  $\text{m}\mu\text{g}$  of lead respectively (st. dev. 6 and 45). Amounts of iron, copper and zinc up to 1000  $\mu\text{g}$  had no influence on these blanks.

#### EXPERIMENTAL METHOD B

See also Method A

##### *Materials and methods*

<sup>204</sup>Tl. Dilute 3.4 mg (1 mC) of <sup>204</sup>Tl(I) with 0.2 N hydrochloric acid to 10 ml and add 22 mg of thallium as Tl<sub>2</sub>SO<sub>4</sub>.

<sup>210</sup>Pb. Dilute 12  $\mu\text{g}$  (0.11 mC) of <sup>210</sup>Pb (Ra - D in equilibrium with its decay products) with 9 N hydrochloric acid to 10 ml.

*Bromine water* (Merck p.a.); *Diethylamine* (May and Baker).

*Cyanide-tartrate solution (a)*: 1% potassium cyanide (AnalaR), 0.02 M ammonium tartrate (AnalaR) and (2x + 0.1) N sodium hydroxide (Merck p.a.) in water. For the value of x see below.

*Cyanide-tartrate solution (b)*: 0.5% potassium cyanide and 0.01 M ammonium-tartrate in water, adjusted (with x gequiv. of sodium hydroxide/l) to pH 11.5.

*Acid Bi-Pb-Tl-carrier*: 1 mg of each metal (nitrates) per ml of 2 N nitric acid.

*Bi-Pb-Tl-DDC-carrier*: 0.5 mg of each metal as the DDC-complex per ml of chloroform.

*DDC-solution*: A fresh solution of 10 mg of DDC in 10 ml of water.

##### *Preparation of <sup>204</sup>Tl-DDC*

The stock solution of <sup>204</sup>Tl-DDC was prepared in chloroform as this solvent showed the smallest back-extraction of <sup>204</sup>Tl during the exchange (see below). The drawback of the co-extraction of DDC was forestalled by using excess <sup>204</sup>Tl for the preparation of the complex.

Again cyanide was used to obtain selectivity. Diethylamine was used as a stabilizer (see below). A 3 weeks-old solution, prepared as indicated below, showed a 2% increase of its radio-activity when shaken with ionic-<sup>204</sup>Tl<sup>+</sup> of the same specific activity, which indicated that after 3 weeks about 2% of the <sup>204</sup>Tl-DDC was decomposed to DDC (or to other molecules able to extract thallium).

*Procedure*: Pipet 1 ml of <sup>204</sup>Tl into a glass tube and neutralize with 2 N ammonia to phenolphthalein. Add 1.1 ml of cyanide-tartrate solution (a) and 2.4 ml of DDC and shake for 3 min at 900 periods per min with 5 ml of chloroform. Centrifuge lightly (1000 r.p.m.; 25 cm Ø) and pipet the aqueous layer into a second tube to repeat the extraction. Strip the collected organic layers 3 times with 2 ml of cyanide-tartrate solution (b), add 1 mmole of diethylamine and adjust the volume to 20 ml. Store in a refrigerator; the solution is stable (enough) for 3 weeks; it contains about 4.0  $\mu\text{C}$  and 100  $\mu\text{g}$  of thallium as <sup>204</sup>Tl-DDC per ml.

##### *Factors influencing the stability of the <sup>204</sup>Tl-DDC*

The instability of the <sup>204</sup>Tl-DDC is a drawback: it brings part of the <sup>204</sup>Tl back into

\* Part of this correction is due to the different detector, and part to the different solvent which is measured.

the aqueous layer during the exchange with lead and thus produces a (variable) blank. The same effect is of course obtained with interfering cations. The influence of several factors on this blank was investigated:

(1) *Organic solvent.* Back-extractions from carbon tetrachloride and *n*-pentanol were higher than from chloroform.

(2) *pH of the sample-solution.* A pH value of 11.5 proved to be optimal for a small blank.

(3) *Concentration of the cyanide.* In order to prevent the interference of foreign cations, 0.5% potassium cyanide had to be added to the sample solution. For amounts of foreign cations below 2  $\mu$ equiv., 0.1% potassium cyanide was sufficient. As the stronger solution did not effect the blank, however, it was chosen for all experiments.

(4) *Temperature.* When the room temperature increased to 25° or above, higher blanks were observed. An alcohol envelope was used to keep the temperature below 20° (Figs. 2 and 3).

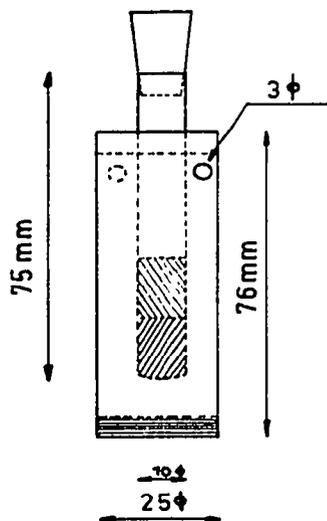


Fig. 2. Polypropylene tube with alcohol envelope.

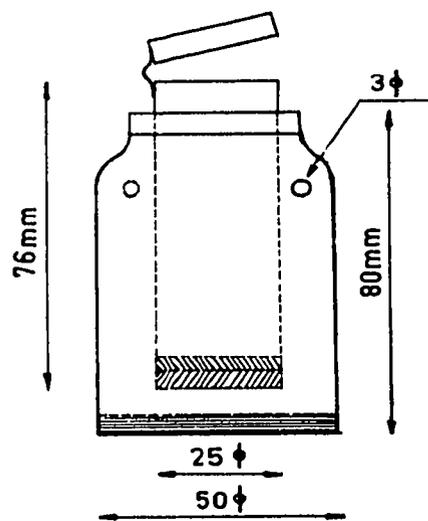


Fig. 3. Polyethylene pill-case with alcohol envelope.

(5) *The influences of (a) the concentration of the  $^{204}\text{Tl}$ -DDC, (b) the volume of both layers, (c) the time and (d) the velocity of the shaker, are all shown in Table III. The cyanide-tartrate solution (b) was used as the aqueous layer. The blank after the second back-extraction is given; the further procedure is described below.*

A shorter shaking-time, a lower velocity, smaller volumes, and a higher concentration of the Tl-DDC are all favourable. Neither a constant amount nor a constant percentage is back-extracted (with any of the treatments).

The variation found in all these blanks might be due to a variation in the polypropylene tubes which are manufactured on metal moulds containing small amounts of lead. Although they are purified thoroughly, small differences in their lead content

might exist. However, the smaller standard deviations (in  $\mu\text{g}$  of  $^{204}\text{Tl}$ ) of the blanks obtained with smaller amounts of  $^{204}\text{Tl}$ -DDC are an indication that this factor is not of much importance.

TABLE III  
BACK-EXTRACTION OF  $^{204}\text{Tl}$  FROM  $^{204}\text{Tl}$ -DDC IN CHLOROFORM  
(Mean values and standard deviations of 8 experiments each)

Treatment <sup>a</sup>	A			B			C			D <sup>b</sup>		
	3-900-1+1			6-900-1+1			6-1400-1+1			6-1400-2+2		
$\mu\text{g}$ of $^{204}\text{Tl}$ as $^{204}\text{Tl}$ -DDC	6	1.5	0.5	6	1.5	0.5	6	1.5	0.5	6	1.5	0.5
$\mu\text{g} \cdot 10^{-3}$ of $^{204}\text{Tl}$ back-extracted	292 <sup>d</sup>	120	55	332	160 <sup>d</sup>	73 <sup>d</sup>	611	352	149	1100	—	—
Standard deviation	20	6	2	21	6	2	176	66	52	360	—	—
% of $^{204}\text{Tl}$ back-extracted <sup>c</sup>	5.3	9.3	13.7	6.3	13.3	19.2	12.2	37.1	49.8	24	>50	<60
Standard deviation	0.36	0.46	0.50	0.39	0.50	0.53	3.5	6.8	17.3	8	—	—

<sup>a</sup> Shaking-time in min (*e.g.* 3), shaking velocity in periods per minute (*e.g.* 900) and volumes of both layers in ml (*e.g.* 1+1).

<sup>b</sup> Carried out in the pill-case of Fig. 3 (the other treatments in the tubes of Fig. 2).

<sup>c</sup> % of the thallium still present as Tl-DDC after the first blank.

<sup>d</sup> Applied in practice.

(6) *Ageing effect of the  $^{204}\text{Tl}$ -DDC.* Older preparations required a preliminary purification: the amounts of thallium back-extracted in the second and third procedures were about equal and were appreciably lower than in the first one. For preparations not older than 2 or 3 weeks, this second or third blank was comparable with the first one of the freshly prepared solution. Evidently decomposition had taken place.

When the addition of diethylamine was omitted, the decomposition increased appreciably. It was not influenced by reducing agents or by a nitrogen atmosphere.

The effect of inactive Tl-DDC or Ag-DDC was only small. As these substances may both be supposed to behave in the same way as  $^{204}\text{Tl}$ -DDC, with respect to the (secondary) effects of the  $\beta$ -radiation, this result shows that radiochemical self decomposition was small. However, with an eight times larger specific activity a distinct radio-decomposition was observed. This solution was only stable for 5 days. The addition of a substance, soluble in chloroform, containing a sulfhydryl group and not extracting lead ions, would probably be favourable for the radiochemical stability but such a substance could not be found. A favourable effect was observed when the complex was stored at  $-5^\circ$  in a benzol-silicagel substrate. Research on this kind of stabilization is in progress.

(7) *Adsorption of  $^{204}\text{Tl}$  ions to the walls.* Apart from the ionic thallium found in the upper layer, 0.45% of the thallium ions were found to be adsorbed to the walls\*. These ions are part of the blank or part of the thallium to be evaluated as being ex-

\* Apart from the adsorption of the  $^{204}\text{Tl}$  ions, adsorption of  $^{204}\text{Tl}$ -DDC itself was observed. This  $^{204}\text{Tl}$ -DDC had to be removed—before the determination of the adsorbed  $^{204}\text{Tl}^+$ —with the help of the Tl-DDC carrier.

changed with lead ions. No influence of the presence of lead ions on the adsorbed amount of  $^{204}\text{Tl}$  was observed and thus this adsorption could be neglected.

#### *Exchange with lead ions*

The influence of the organic solvent, the pH\*, the concentration of the cyanide, and the age of the  $^{204}\text{Tl}$ -DDC, on the rate of exchange, proved to be small. On the other hand, higher temperatures, shaking velocities and concentrations of both components, were favourable for a high rate of exchange. No use of the first two factors could be made, however, because of the higher blank.

With the procedure given below the exchange between 0.5  $\mu\text{g}$  of lead in water and 6  $\mu\text{g}$  of thallium as  $^{204}\text{Tl}$ -DDC in chloroform proved to be efficient only to 60–70%. A 25-fold excess of thallium was required for 90% exchange. It is evident (Table III) that the error caused by the variation of the blank then becomes too high. Isotope dilution with  $^{210}\text{Pb}$  was introduced and the amount of  $^{204}\text{Tl}$  in the aqueous layer was taken as a measure of the exchanged amount of lead.

#### *Isotope dilution with radio-active lead*

When a radio-isotope of lead is introduced, it has to be measured in presence of  $^{204}\text{Tl}$  (which is the only suitable radio-isotope of thallium).  $^{212}\text{Pb}$  (Th-B) can be separated from a thorium source, but not from its decay products (owing to their short half-life). Measurement of  $^{204}\text{Tl}$  in the presence of these decay-products is impossible.  $^{210}\text{Pb}$  (Ra-D) can be separated from a radium source and also from its decay products. Measurement of  $^{210}\text{Pb}$  and  $^{204}\text{Tl}$  in the presence of each other is feasible.

$^{210}\text{Pb}$  was separated from its decay products ( $^{210}\text{Bi}$  and  $^{210}\text{Po}$ ) by anion exchange. The technique consisted in the sorption of the latter two elements from 9 *N* hydrochloric acid in a column (5 cm high, 0.27 cm<sup>2</sup> in diameter) of Dowex 1X10 – 100 to 200 mesh. About 98, 1 and 10% of the three isotopes respectively were found in the eluate; the influence of Pb and Bi carriers was negligible.  $^{210}\text{Po}$  does not influence the measurements of  $^{210}\text{Pb}$  and  $^{204}\text{Tl}$  to a large extent. The  $^{210}\text{Bi}$  influences both measurements, but corrections can be made.

$^{210}\text{Bi}$ , when carrier-free, exchanged with  $^{204}\text{Tl}$  at a lower rate than the lead. This is not in accordance with the sequence of affinities to DDC, and is obviously due to the extremely low concentration of the bismuth. As a consequence, the ratio  $^{210}\text{Bi}/^{210}\text{Pb}$  changed during the exchange with  $^{204}\text{Tl}$ . A small correction is made for this phenomenon.

#### *Measurement of $^{204}\text{Tl}$ and $^{210}\text{Pb}$*

The GM-tube was preferred for the measurement of  $^{204}\text{Tl}$ , as its correction factor for  $^{210}\text{Pb}$  ( $^{210}\text{Bi}$ ) was more favourable than with our crystal.

Measurement of the exchanged percentage of lead in the organic layer had to be avoided as this layer generally contained a large excess of  $^{204}\text{Tl}$ . Thus the aqueous  $^{210}\text{Pb}$  was measured (with the crystal, at the 47 keV-maximum). As about 2% of the lead is adsorbed to the wall during the exchange procedure, the percentage of aqueous  $^{210}\text{Pb}$  was subtracted from 98 to find the exchanged percentage.

As indicated above, the measurement of  $^{204}\text{Tl}$  had to be corrected with the help

\* Between pH 8.5 and 13.5. This is in contrast to the exchange of  $^{204}\text{Tl}^{+3}$  with  $\text{Pb}-(\text{DDC})_2$  (see method A).

of the "GM%" of  $^{210}\text{Pb}$ - $^{210}\text{Bi}$  (10 to 15). On the other hand the measurement of  $^{210}\text{Pb}$  had to be corrected for  $^{204}\text{Tl}$  ("channel%" about 5 to 7).

With all measurements at least 1000 counts were registered. Including the errors in the correction factors, the total error was about 5%.

#### PROCEDURE FOR METHOD B

The procedure is given for a sample containing from 0.1 to 0.6  $\mu\text{g}$  of lead and (per  $\mu\text{equiv.}$ ) not more than the following amounts of foreign ions (also in  $\mu\text{equiv.}$ ):  $\text{Bi}^{+3}$  and  $\text{Tl}^{+3}$  0.1;  $\text{Fe}^{+3}$  6,000;  $\text{Cu}^{+2}$ ,  $\text{Hg}^{+2}$  and  $\text{Ag}^{+}$  8,000; other heavy metal ions 28,000;  $\text{P}_2\text{O}_7^{-2}$  15,000 and  $\text{PO}_4^{-3}$  15,000.

#### Daily standardizations

Standardize  $^{204}\text{Tl}$  and determine the "channel%". Purify  $^{210}\text{Pb}$ , standardize and neutralize with ammonia to bromocresol purple (pH 1.0). Correct the volume to a 2-fold of the original  $^{210}\text{Pb}$ -solution. Determine the "GM%" at the time of the measurement of the samples (see below) and, when the exchanged percentage of lead is larger than 20, add 1.8 to this "GM%" (because of exchange of Bi).

#### Weekly determination of the blank

Check the  $^{204}\text{Tl}$ -DDC for losses by adsorption to the wall: transfer an aliquot containing about 1.5  $\mu\text{g}$  of  $^{204}\text{Tl}$  to a tube (Fig. 2) and adjust the volume with chloroform to 1 ml. Add 1 ml of cyanide-tartrate solution (b), shake for 6 min at 900 p.p.m. and centrifuge for 1 min (1000 r.p.m.;  $\varnothing$  25 cm). Remove the aqueous layer and rinse the chloroform with a second 1-ml portion of cyanide-tartrate solution (b). Repeat the blank; this second time dilute the collected aqueous layers with the acid Bi-Tl-Pb-carrier to 10 ml and measure in the M6-GM-tube.

#### Determination of 0.1 to 0.6 $\mu\text{g}$ of lead

Dissolve the sample in nitric and/or hydrochloric acid and evaporate to about 0.2 ml; then add 0.02 ml of the neutralized  $^{210}\text{Pb}$ -solution, neutralize with concentrated ammonia to bromocresol purple and adjust the volume to 0.5 ml. Now carry out the procedure for the blank, but instead of the third 1-ml portion of cyanide-tartrate solution (b), add 0.5 ml of cyanide-tartrate solution (a). Then add the neutralized sample and carry out the further procedure for the blank as given above. To the collected aqueous layers add only 1 ml of the acid carrier, however, and measure the  $^{210}\text{Pb}$  in 1 ml of the mixture. Determine the remaining volume by suction in a pipet, dilute with the acid Bi-Tl-Pb-carrier to 10 ml and measure the radio-activity of  $^{204}\text{Tl}$  in the GM-tube. Carry out the calculation as indicated above. Correct the amount of lead found in this way for the lead in the  $^{210}\text{Pb}$  (0.010  $\mu\text{g}$ ).

For the determination of 0.6 to 3.0  $\mu\text{g}$  of lead use the same amount of  $^{210}\text{Pb}$  as above, but 6  $\mu\text{g}$  of  $^{204}\text{Tl}$  as  $^{204}\text{Tl}$ -DDC. A shaking time of 3 min is sufficient. For 0.05 to 0.15  $\mu\text{g}$  of lead use only 0.005 ml of the neutralized  $^{210}\text{Pb}$ -solution and only 0.5  $\mu\text{g}$  of  $^{204}\text{Tl}$  as  $^{204}\text{Tl}$ -DDC.

#### RESULTS WITH METHOD B

The values of the blanks are given in Table III, footnote 4. Some results with standard

TABLE IV  
DETERMINATION OF 0.05 TO 0.6  $\mu\text{g}$  OF LEAD WITH  $^{204}\text{Tl}$ -DDC

I	2	3	4	5	6	7	8	9	10	11
Experiment No.	Lead added <sup>a</sup> ( $\mu\text{g} \cdot 10^{-3}$ )	$^{204}\text{Tl}$ used as $^{204}\text{Tl}$ -DDC ( $\mu\text{g} \cdot 10^{-3}$ )	Lead exchanged (%)	$^{204}\text{Tl}$ exchanged <sup>b</sup> ( $\mu\text{g} \cdot 10^{-3}$ )	Lead exchanged (from column 5) ( $\mu\text{g} \cdot 10^{-3}$ )	Lead found (from columns 4 and 6) ( $\mu\text{g} \cdot 10^{-3}$ )	Mean value of column 7	Standard deviation ( $\mu\text{g} \cdot 10^{-3}$ )	Error of mean (%)	Standard deviation (%)
1	600	1500	43	476	245	570	593	46	-1	8
2	600	1500	42	496	255	608				
3	600	1500	40	506	260	650				
4	600	1500	48 <sup>a</sup>	514	264	545				
5	300	1500	26	176	90	346	322	24	+7	7 <sup>b</sup>
6	300	1500	27	153	78	289				
7	300	1500	30	190	97	323				
8	300	1500	38	245	125	328				
9	100	1500	26	56	28 <sup>a</sup>	110	96 <sup>b</sup>	9 <sup>b</sup>	-3 <sup>b</sup>	9 <sup>b</sup>
10	100	1500	45	85	43	95 <sup>b</sup>				
11	100	1500	45	80	40 <sup>a</sup>	90				
12	100	1500	29	51	26	90				
13	150	500	18	50	25 <sup>a</sup>	142				
14	150	500	20	58	29 <sup>a</sup>	148	142	10	-5 <sup>b</sup>	7 <sup>b</sup>
15	150	500	21	62	31 <sup>a</sup>	150				
16	150	500	24	60	30 <sup>a</sup>	127				
17	100	500	20	44	22 <sup>a</sup>	112	112	9 <sup>b</sup>	+6	9
18	100	500	24	53	27	112				
19	100	500	28	53	27	96 <sup>b</sup>				
20	100	500	30	55	28	93 <sup>b</sup>				
21	50	500	18	19	9 <sup>a</sup>	53	51	6	+2	12
22	50	500	22	24	12	54 <sup>a</sup>				
23	50	500	26	27	14	54				
24	50	500	24	20	10	41 <sup>a</sup>				

<sup>a</sup> Including the lead in the  $^{210}\text{Pb}$

<sup>b</sup> After subtraction of the blank

amounts of lead are given in Table IV. The amounts of lead added are compared with the values calculated from the exchanged amount of thallium and the exchanged percentage of lead.

#### DISCUSSION OF METHODS A AND B

(A) The blank value is mainly determined by the "DDC-blank" and the "Tl-blank". The former evidently does not reach its theoretical value, owing to an incomplete reaction between DDC and  $^{204}\text{Tl}^{+3}$ . To obtain a higher sensitivity however, the cyanide should be purified without the use of DDC (MAYNES AND MCBRYDE<sup>15</sup>) or the "AnalaR" product should be used (see B).

The standard deviation is due to variations in the blank, the efficiency of the process and the measurement of  $^{204}\text{Tl}$ . Better results could perhaps be attained by (1) using AnalaR potassium cyanide; (2) evaporation of the carbon tetrachloride before the exchange (both (1) and (2) resulting in a smaller "DDC-blank"); (3) a higher excess of  $^{204}\text{Tl}$ ; (4) prolonged shaking times (both (3) and (4) resulting in a higher efficiency of the process) and finally (5) introduction of isotope dilution with  $^{210}\text{Pb}$  to evaluate the efficiency.

(B) The blank value has already been discussed. Only the radiochemical self-decomposition could not be controlled. The blank cannot be lowered by decreasing the excess of Tl-DDC as the actual blank in the experiment would become smaller than the blank determined with the omission of lead.

The standard deviation is due to variations in (1) the blank and (2) the measurement of both isotopes. The influence of both factors increases with smaller amounts of lead: (1) a higher excess of Tl-DDC is required for a reasonable exchange, (2) either the counting error or the self-decomposition increases.

Method B is twice as sensitive as method A and 4, 10 and 20 times more sensitive than the spectrographic, polarographic and spectrophotometric techniques respectively. In addition, it requires only 40 min (30 working min) for a duplicate, which is about twice as quick as method A. Finally larger amounts of (most) foreign ions are permitted. Method A is to be preferred, however, when the sample contains small amounts of bismuth and/or thallium. Larger amounts of these metals should be removed in advance for both methods A and B. Anion exchange in 9 *N* hydrochloric acid is attractive for this purpose; thallium(I) should be oxidized to thallium(III) (see KRAUS AND NELSON<sup>16</sup>).

Both procedures A and B seem to be adaptable for the determination of other cations.

#### ACKNOWLEDGEMENT

The author is indebted to Mrs. W. CLINÉ-THEIL and Miss J. H. F. F. BROEKMAN for valuable technical assistance.

#### SUMMARY

Two methods for the determination of submicrogram amounts of lead are described. (A) Lead is selectively extracted with carbon tetrachloride from an alkaline solution containing excess diethyl-dithiocarbamate (DDC) and cyanide. Traces of DDC are back-extracted. The lead in the DDC complex is exchanged with  $^{204}\text{Tl}$  and the amount of  $^{204}\text{Tl}$  in the organic layer acts as a measure for the lead. The limit of sensitivity is 0.1  $\mu\text{g}$ ; the standard deviation is 11% (for 0.1  $\mu\text{g}$ ). Bismuth and thallium interfere; their influence can be accounted for with the help of EDTA, however.

(B) Excess cyanide is added to the alkaline sample solution and lead is exchanged selectively with  $^{204}\text{Tl}$  by shaking with a  $\text{CHCl}_3$  solution containing  $^{204}\text{Tl}(\text{DDC})_1$ . As the process is not 100% effective (with a reasonable excess of the thallium complex) isotope dilution with  $^{210}\text{Pb}$  is also carried out. The amount of  $^{204}\text{Tl}$  in the aqueous layer acts as a measure for the exchanged lead. The limit of sensitivity is  $0.05 \mu\text{g}$  and the standard deviation is 12% (for  $0.05 \mu\text{g}$ ). Bismuth and thallium must be removed in advance, e.g. by anion exchange.

## RÉSUMÉ

Deux méthodes sont proposées pour le dosage radiochimique de traces de plomb: (A) Le plomb est extrait dans le tétrachlorure de carbone en présence de diéthylthiocarbamate et de cyanure en solution alcaline. On procède ensuite par échange du plomb extrait par le thallium-204. La mesure de  $^{204}\text{Tl}$  dans la phase organique permet de déterminer la teneur en plomb. (B) On procède par échange direct du plomb au moyen du thallium-204, par traitement avec une solution de diéthylthiocarbamate de thallium-204 dans le chloroforme.

## ZUSAMMENFASSUNG

Spuren von Blei können radiochemisch nach 2 Methoden bestimmt werden: (A) Man extrahiert das Blei in Gegenwart von Diäthylthiocarbamat und KCN mit Tetrachlorkohlenstoff. Durch Schütteln mit einer  $^{204}\text{Tl}$ -Lösung wird das Blei durch  $^{204}\text{Tl}$  substituiert. Der  $^{204}\text{Tl}$  Gehalt in der organischen Phase entspricht dem Bleigehalt. (B) Man schüttelt die mit KCN versetzte Probelösung mit einer Chloroformlösung von  $^{204}\text{Tl}$ -Diäthylthiocarbamat und bestimmt in der wässrigen Phase den Gehalt an  $^{204}\text{Tl}$ .

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