

## QUANTITATIVE INORGANIC CHROMATOGRAPHY

PART IV. THE SEPARATION AND DETERMINATION OF SOME  
HEAVY METALS IN ADMIXTURE WITH LEAD \*

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Although many paper chromatographic procedures<sup>1-11</sup> have been published for the separation of lead from other heavy metals, these have been mainly concerned with the qualitative separation of the Groups I and IIA of the general qualitative analytical scheme. Such separations, although invaluable for qualitative purposes, are unsuited for quantitative chromatography where complete separations are usually required. LEWIS AND GRIFFITHS<sup>12</sup> showed how problems in polarographic analysis were overcome by paper chromatography. The eluting solvent employed was 5% v/v concentrated hydrochloric acid (1.18) in *n*-butanol; after elution and extraction the lead was estimated polarographically in the presence of vanadium, copper, uranium, and titanium. Unfortunately the polarographic method used was of low sensitivity and for accurate results great care was needed. For the estimation of lead in natural waters, CARRITT<sup>13</sup> passed the sample down a column composed of a solution of diphenylthiocarbazone in carbon tetrachloride absorbed on cellulose acetate. Heavy metals were absorbed as their respective dithizonates. The column was then stripped of cadmium, zinc, manganese, and lead by treatment with 1 *M* hydrochloric acid and these metals were simultaneously estimated polarographically. HUNT, NORTH AND WELLS<sup>14</sup>, separated other metals from lead using paper strips and eluting with 5% v/v concentrated hydrochloric acid (1.18) in methanol. The method was applied to the semi-quantitative estimation of lead in soils.

The work to be described was undertaken in an attempt to resolve simultaneously the following analytical problems:

(1) The lengthy procedure necessary for the isolation and accurate determination at  $\mu\text{g}$  level of more than one heavy metal ion on the same sample of solution<sup>15-18</sup>. In general the published analytical procedures show a number of methods but most of these are designed for the estimation of one element per aliquot of sample solution taken. Thus when a mineral analysis for four or five elements is required, the time taken to complete such a task is prohibitive, and often only a small quantity of material is available<sup>19</sup>.

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\* For parts I, II and III, see ref. 23, 24, 27 respectively.

(2) The complications and errors incurred when employing diphenylthiocarbazono for the extraction and absorptiometric estimation of lead<sup>20, 21</sup>.

(3) The lack of data concerning the quantitative chromatographic behaviour of the lead ion.

#### APPARATUS AND GENERAL TECHNIQUE

The downward elution method was used, the apparatus for which has been described previously<sup>22-24</sup>. The all-glass apparatus consisted of two troughs (24 cm long by 2.5 cm in diameter) supported on a glass stand contained in a tank (23 cm × 28 cm and 52 cm deep) the top of which was smeared with grease, and covered with a ground-glass plate drilled with two holes located one over each trough. The purpose of these holes was to permit solvent to be admitted into the trough without disturbing the equilibration of the tank. The solvent mixture used for equilibrating the tank and for elution had the same composition.

The Whatman No. 1 filter-paper used for the chromatographic separation was purified by acid washing for six days and then washed free from chloride with distilled water<sup>23, 25</sup>. The paper chromatogram bearing the metals to be separated was placed in position in one of the troughs, solvent was poured into the other trough and into the bottom of the tank, the apparatus being left to equilibrate overnight. Solvent was poured into the trough containing the chromatogram through the hole in the cover plate and the solvent allowed to percolate 35 cm down the paper. The chromatogram was then removed, dried and sprayed.

#### *The eluting solvent*

In quantitative chromatography it is necessary to use metal salts corresponding to the acid species in the solvent in order to prevent the metal ions from forming more than one spot<sup>26</sup>. The salts chosen in this case were the metal nitrates since all of them (where nitrates exist) have the common property of being soluble in water. Consequently if the eluting solvent contains dilute nitric acid, true "partition" chromatography may occur and not precipitation chromatography, *i.e.* the precipitation of an insoluble salt near the starting line due to the presence in the solvent of an anion of an acid capable of forming such a salt with the metal ion under investigation. In many such cases the insoluble salt streaks forward due to the slight solubility of the precipitated salt in the solvent as it percolates over the band. This causes low recovery values to be obtained unless special precautions are taken.

The solvent system for the separation of lead, zinc, and mercuric mercury on acid-washed Whatman No. 1 filter-paper was developed by A. J. BANISTER of these laboratories, employing the semi-graphical technique and ascending elution<sup>27</sup>. The solvent A finally selected, consisted of 50 ml diethyl ether, 30 ml methanol, 20 ml water, and 2 ml of AnalaR nitric acid (1.42). To determine the  $R_F$  values of the heavy metal ions under consideration in this solvent but employing descending elution, a series of chromatograms were eluted using single spots of the aqueous metal nitrates (each spot contained approx. 15  $\mu\text{g}$  of the metal). The chromatograms

TABLE I

<i>Metal ion</i>	<i>Spray</i>	<i>Colour of spot</i>	<i>R<sub>F</sub> value (head and tail of spot)</i>
Tl(I)	0.5% w/v 8-hydroxyquinoline in absolute alcohol. Hold over ammonia and u.v. light.	Yellow-green fluorescence	0.25-0.17
Ag(I)	5% w/v tannic acid in warm 60% v/v aqueous methylated spirits. Warm the damp strip.	Brown stain	0.36-0.27 Dark hydrolysis products also present at starting line
Pb(II)	Aqueous solution of rhodizonic acid and held over ammonia.	Red	0.41-0.22
Zn(II)	0.5% w/v 8-hydroxyquinoline in absolute alcohol. Hold over ammonia and under u.v. light.	Yellow fluorescence	0.66-0.55
Cd(II)		Yellow fluorescence	0.66-0.55
Cu(II)	0.1% w/v rubeanic acid in absolute alcohol. Hold over ammonia.	Green	0.66-0.56
Co(II)		Yellow-brown	0.68-0.55
Ni(II)		Blue	0.68-0.55
Mn(II)	4% v/v salicylaldehyde in 50% aqueous ethyl alcohol. Hold over ammonia and under u.v. light.	Dark spot against a yellow-green fluorescent background	0.70-0.56
Fe(II)	0.5% w/v aqueous potassium ferrocyanide.	Blue	0.70-0.58
Fe(III)		Blue	0.70-0.58
Bi(III)*	10% w/v freshly prepared aqueous sodium dithionite. Warm.	Brown	Hydrolysed all down the paper to 0.8
U(VI)	0.5% w/v aqueous potassium ferrocyanide.	Brown	0.78-0.72
Hg(II)	0.05% w/v dithizone in chloroform.	Pale pink	0.95-0.87

\* Bismuth may be chromatographed successfully only if the original solution contained 5% v/v aqueous nitric acid, then no hydrolysis products are formed, and the  $R_F$  value of Bi is 0.78-0.67.

after elution were cut up and each strip sprayed with a sensitive reagent for the detection of the respective metal ion. Table I shows the  $R_F$  values of the metal ions chromatographed and the spray reagents employed for their detection. From Fig. 1 it may be seen that it is possible to separate completely the heavy metals of major interest (*i.e.* Zn(II), Cd(II), Cu(II), Fe(II), Ni(II), Bi(III), Hg(II)) from lead (Pb(II)) but the complete separation of lead, thallous thallium, and silver is impossible. Bismuth is only eluted satisfactorily when the applied spot contains 5% v/v nitric acid, but unfortunately ferric iron and bismuth overlap, if applied simultaneously to the chromatogram. A further investigation was then carried out to overcome this difficulty, and the solvent B selected was 50 ml diethyl ether, 30 ml methanol, 22 ml water and 4 ml of AnalaR nitric acid (1.42). (See Fig. 2.) When bismuth is present, solvent B must be used but for all other purposes solvent A is satisfactory.

### Purity of materials

In the preliminary work on the estimation of lead, considerable difficulty was encountered due to the presence of lead, and other trace heavy metals in materials and apparatus used.

(a) *Apparatus.* Trace metals including lead are readily removed from porcelain or silica apparatus by boiling acids, so extraction techniques were developed which used only Pyrex glass vessels. The danger of "pick-up" was thus minimised and all apparatus was cleaned out with hot 10% caustic soda solution, followed by hot 1:1 aqueous nitric acid and copious washings with distilled water.

(b) *Water.* Water from a single distillation using a metal still was found to contain a fairly high percentage of heavy metals, usually of the order of 0.1 mg per litre. A

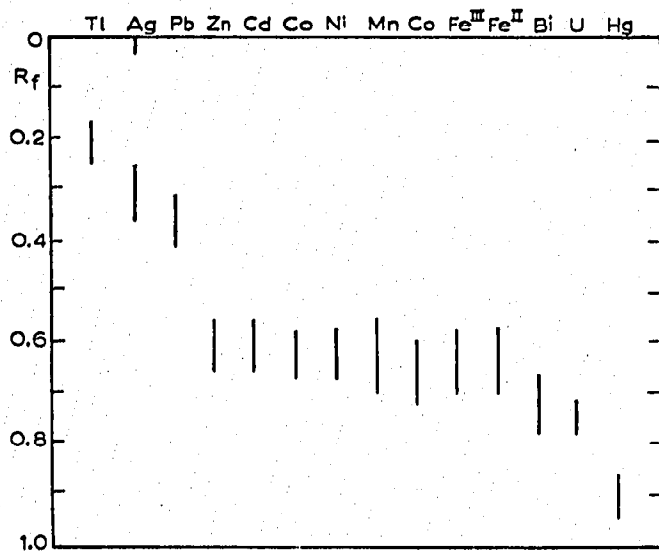


Fig. 1. The  $R_f$  values of 14 cations in descending elution with the solvent system  $\text{Et}_2\text{O}-\text{MeOH}-\text{H}_2\text{O}-\text{HNO}_3$ ; 50:30:20:2 (Solvent A).

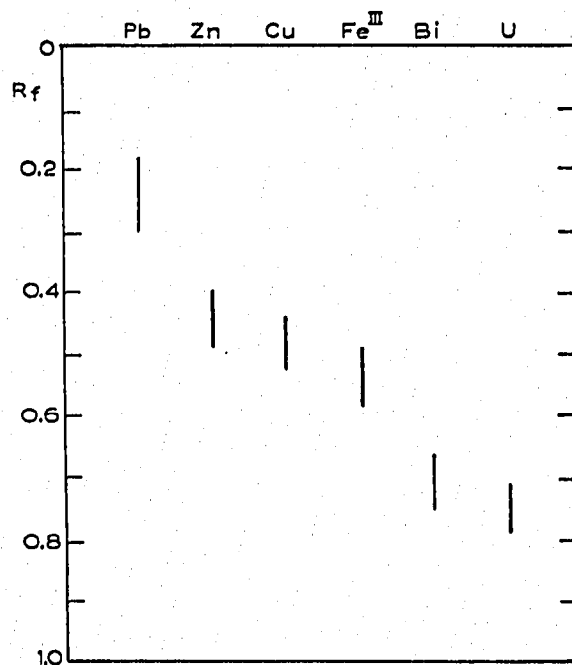


Fig. 2. The  $R_f$  values of 6 cations in the solvent system  $\text{Et}_2\text{O}-\text{MeOH}-\text{H}_2\text{O}-\text{HNO}_3$ ; 50:30:22:4 (Solvent B).

double distillation from a steamed out all-glass (Pyrex) apparatus and storage in Jena glass vessels reduced this figure to approximately 0.01 mg per litre.

(c) *Components of the solvent.* The organic components of the solvent were tested for their heavy metal content, using the dithizone method for lead<sup>21</sup> on the residue left after evaporation of the organic phase. The level of metal content was less than 0.05  $\mu\text{g}$  of heavy metals per ml.

The lead content of the acid is relatively high, 2  $\mu\text{g}$  of lead per ml, but the error involved was considered negligible since it is present only up to 4% by volume in the eluting solvent.

(d) *The filter-paper.* The problem of impurities in filter-paper has been discussed in some detail previously<sup>23, 27</sup> and will only be mentioned briefly. Iron is the major

heavy metal impurity, the general content of Whatman No. 1 paper being  $0.1 \mu\text{g}$  of iron per  $\text{cm}^2$ , this value may be decreased to  $0.02 \mu\text{g}$  per  $\text{cm}^2$  by acid washing but complete removal of iron is extremely difficult except by such treatment that destroys the fibrous nature of the paper. Many procedures were studied for the complete removal of iron but it appears that the solvent continuously dissolves away very small quantities of the cellulose during elution and thus sets free metallic impurities not previously removed in the washing procedure.

Great care must be taken over the storage of filter paper since iron pick-up from dust of the atmosphere over a period of time occurs very rapidly indeed. The method of purification of the paper has been described above (p. 285).

#### *Design of quantitative chromatogram*

Two main types of quantitative chromatogram were again used<sup>24</sup>.

(1) *The wide band strip*<sup>28</sup>. A sheet of paper 20 cm by 55 cm was employed with the starting line marked 10 cm from the upper narrow edge. The solution to be chromatographed was applied as a band 12 cm long by 1 cm wide along the starting line from a calibrated Agla micrometer syringe. Spots of solution (approx. 0.02 ml) were applied 3 cm from the edges of the band. After elution two strips 3 cm wide were cut (one from each edge of the chromatogram) and sprayed for the metals under investigation. The pilot strips were then used as guides for the metal-bearing sections of the main chromatogram.

(2) *Twin paper strips*. The chromatogram consists of twin strips each 4 cm wide and 50 cm long divided by a 0.5 cm slot<sup>23,24</sup>. Identical volumes of solution were delivered along the two sections of the starting line, the wet bands being no wider than 1.5 cm. For larger volumes, the solution was put on the chromatogram in successive 0.025 ml portions, the chromatograms being dried with an electric dryer between each addition. After elution, one strip was then sprayed to locate the ions while the other was used for the estimations.

The second type of chromatogram was favoured for quantitative estimations for the reasons discussed in detail elsewhere<sup>24</sup>. To concentrate a smaller quantity of one metal in the presence of a large amount of another metal which moves to a lower  $R_F$  value, a tapered twin-strip chromatogram was used. The strips were tapered from a width of 4 cm to a width of 2 cm at a distance of 20 cm from the starting line. The width is constant (2 cm) for the lower 30 cm of the strips. By this means the metals are concentrated into a smaller area of paper, for which the blank correction is consequently less.

#### *Extraction of metals from the chromatogram*

Many extraction procedures were investigated for each metal ion but in general only (1) complete wet digestion of the paper by the conventional means for destroying organic material<sup>29</sup>, or (2) acid leaching at an elevated temperature<sup>30</sup>, gave quantitative recovery values. The disadvantage of method (1) is the time required in order to obtain a white ash residue and only method (2) will be described in detail.

(a) *Lead*. The section of the chromatogram containing lead was cut up into small pieces, placed in a 100 ml Pyrex beaker, covered with 10 ml of 2 *M* nitric acid and the solution boiled for 1 min. The extract was decanted off and stored. The extraction procedure was then repeated employing (1) 10 ml of 1 *M* nitric acid and (2) 10 ml of distilled water. The three extracts were combined, filtered through a Jena No. 3 sintered glass crucible and finally evaporated down to very small bulk using surface heating.

(b) *Bismuth*. Bismuth may be extracted by a procedure similar to (a) except that perchloric acid is employed in place of nitric acid.

(c) *Cadmium, copper, iron, and zinc*. If only one of these ions is present in the mixture extraction using a procedure similar to (a) but employing hydrochloric acid instead of nitric acid results in quantitative recovery. If, however, two or more ions are present, they will be fully separated from lead but not from each other since their  $R_F$  values are similar (Table I). Extraction with dilute hydrochloric acid on the metal-bearing section of the paper still yields quantitative recovery values but for individual estimation of each element a further separation has to be carried out (by anion exchange chromatography).

#### *Anion-exchange separation of cadmium, copper, iron, and zinc*

KRAUS AND MOORE<sup>31</sup> succeeded in separating the transition elements (manganese to zinc) in hydrochloric acid solutions by anion-exchange chromatography employing Dowex-1 resin. The adsorbabilities of these elements differ sufficiently as a function of the hydrochloric acid concentration to permit their ready separation at the mg level of concentration. RUSH AND YOE<sup>32</sup> using the same type of resin reported a separation of copper(II) and iron(III) from zinc(II) at microgram level. Copper(II) and iron(III) are eluted by 1 *M* hydrochloric acid while zinc is strongly adsorbed, zinc is later eluted from the column with 0.005 *M* hydrochloric acid. HUNTER AND MILLER<sup>33</sup> separated zinc from numerous other elements by anion-exchange in dilute hydrochloric acid using Amberlite IRA-400, in the concentration range 0.1–5 mg of zinc. KALLMANN, STEELE AND CHU<sup>34</sup> reported a separation of zinc and cadmium in dilute hydrochloric acid-sodium chloride solutions using Dowex-1 resin from most of the elements associated with zinc or cadmium. Zinc was quantitatively separated from cadmium by elution with 2 *M* caustic soda containing 20 g of sodium chloride/l, the cadmium was later eluted from the column with 1 *M* nitric acid. Unfortunately, no details of a separation of Fe(III), Cu(II), Zn(II), and Cd(II) at mg level was found in the literature. Since the elution constants of these elements are already available<sup>31, 34</sup> only the practical details for the separation will be given.

*Apparatus*. The column consisted of a glass tube 15 cm long, 0.5 cm radius fitted with a 2 mm glass tap at the lower end, and packed to a depth of 10 cm with Amberlite IRA-400 resin of 150 mesh size. The eluting agent was passed through the column using a 50 cm head of liquid. The column was purified by passage of several hundred ml of 1 *M* nitric acid, followed by copious washings with distilled water. The resin was then saturated with 3 *M* hydrochloric acid in readiness for use.



titration with EDTA. The purpose of the investigation was to see if it was possible to use this type of reaction and colorimetrically estimate the magnesium with Eriochrome Black T.

Employing the method due to POLLARD AND MARTIN<sup>36</sup> and adding 5.0 ml of 0.01 *M* magnesium-EDTA complexonate solution, a satisfactory method for the estimation of lead was developed. Beer's law is obeyed over the range 0-10  $\mu\text{g}$  of lead per ml, and the slope of the calibration graph was 0.105 optical density units per  $\mu\text{g}$  of lead per ml at 520  $\text{m}\mu$ . Although this method is only one-third as sensitive as the dithizone method, it is preferred since it can be carried out in aqueous solutions. When copper, zinc, mercury, cadmium, or silver are present with lead, they may be effectively masked by the addition of potassium cyanide solution. The interference of iron and cobalt, however, cannot be eliminated since their cyanide complexes tend to oxidise Eriochrome Black T irreversibly when in strongly alkaline solution.

This method was used for the work on the binary and ternary mixtures of the heavy metals containing lead, but has recently been superseded by the method described below.

(b) *4-(2-Pyridylazo)-resorcinol*. This reagent has been synthesized in these laboratories and is especially noteworthy in that it forms a water-soluble chelate with lead salts which is suitable for spectrophotometric estimation of lead. Details of the synthesis and general properties of the reagent are described in a paper published elsewhere<sup>37</sup>, and only details of the method for the estimation of lead will be described.

To the neutral sample containing between 0-125  $\mu\text{g}$  of lead in a 25 ml volumetric flask are added 2.0 ml of 0.05% w/v aqueous 4-(2-pyridylazo)-resorcinol solution, 10 ml of buffer pH 10 (ammonium chloride in aqueous ammonium hydroxide solution) and the mixture diluted to 25 ml. The optical density of the solution is measured at 530  $\text{m}\mu$  against a similarly prepared blank solution containing no lead.

Beer's law is obeyed over the range 0-5  $\mu\text{g}$  of lead per ml, and the slope of the calibration graph at 530  $\text{m}\mu$  is 0.165 optical density units per  $\mu\text{g}$  of lead per ml. This method was used for the lead analyses given in Tables II, III and IV.

### *Bismuth*

After evaporation of the extract to a few ml, this solution was ready for absorptiometric analysis using the thiourea method described by LISICKI AND BOLTZ<sup>38</sup>.

### *Iron*

The boiled-down solution (or aliquot of the same) was transferred to a 25 ml volumetric flask. 2.0 ml of 5% w/v aqueous hydroxylamine hydrochloride solution was added, followed by 1 drop of 0.05% w/v aqueous methyl orange, and 0.5 *M* caustic soda solution until the indicator just turned yellow. Finally 1.0 ml of 0.247% w/v aqueous 2-nitroso-1-naphthol-4-sulphonic acid (sodium salt), together with 3.0 ml of 0.20 *M* acetic acid and 7.0 ml of 0.20 *M* sodium acetate solution were added. The solution was diluted to the correct volume and its optical density measured at 700  $\text{m}\mu$  against a similarly prepared reagent blank<sup>27</sup>.



Beer's law is obeyed over the range 0-4  $\mu\text{g}$  of iron/ml and the slope of the calibration graph is 0.428 optical density units per  $\mu\text{g}$  of iron per ml.

### Copper

(a) *Biscyclohexanone oxalyldihydrazone*. The boiled-down copper solution was transferred to a 25 ml volumetric flask and its copper content estimated by the procedure described by PETERSON AND BOLLIER<sup>39</sup>.

(b) *Zincon*. The boiled-down copper solution was neutralised to approximately pH 5 employing methyl orange and 0.5 *M* caustic soda solution. The copper content was estimated employing the procedure described by RUSH AND YOE<sup>32</sup>.

### Zinc

(a) *Eriochrome Black T*. Zinc may be estimated by a procedure exactly similar to that described for the indirect estimation of lead employing Eriochrome Black T. The slope of the calibration graph is 0.335 optical density units per  $\mu\text{g}$  of zinc per ml at 520  $m\mu$ .

(b) *Zincon*. The boiled-down zinc solution was neutralised to about pH 9 by addition of 2 drops of 0.05% w/v neutral red solution, and 0.5 *M* hydrochloric acid until the indicator just changed from red to yellow. The procedure described by RUSH AND YOE<sup>32</sup> for the estimation of zinc using *Zincon* was employed.

### Simultaneous estimation of copper and zinc with *Zincon*

If only copper and zinc are present then they may be estimated in the manner described by RUSH AND YOE<sup>32</sup>. Maximum absorption of the copper complex occurs at 610  $m\mu$ , and the pH range for formation is 4.5-10. The zinc complex also exhibits maximum absorption at 610  $m\mu$ , but is only formed above pH 8. Hence, RUSH AND YOE<sup>32</sup> estimated the copper content of the sample on an aliquot of solution at pH 5.2, whilst another estimation at pH 9 gave the combined zinc-copper figure; the zinc figure was obtained by difference.

The present work confirmed the possibility of simultaneously estimating zinc and copper but a slight modification was required. RUSH AND YOE observed that the slopes of the calibration graphs for copper at pH 5.2 and 9.0 were the same, hence the zinc was obtained by direct difference. For this work it was found that the slope of the calibration graph for copper at pH 5.2 was slightly lower than that at pH 9.0. A correction has thus to be made to convert the optical density reading for copper alone at pH 5.2 into an equivalent reading at pH 9.0. If this is done, the zinc figure may be accurately found by difference. The slopes of the calibration graphs for copper at 610  $m\mu$  are (1) 0.370 optical density units per  $\mu\text{g}$  of copper per ml at pH 5.2 and (2) 0.382 optical density units per  $\mu\text{g}$  of copper per ml at pH 9.0.

### Cadmium

The residue after elution and fuming down to a few drops was dissolved in 5 ml of 0.01 *M* hydrochloric acid, this solution was transferred to a 100 ml volumetric flask for absorptiometric determination.

TABLE II  
SEPARATION OF LEAD, COPPER, IRON AND ZINC

Ratio Pb:Zn:Cu:Fe	Lead		Zinc		Copper		Iron	
	present μg	found μg	present μg	found μg	present μg	found μg	present μg	found μg
1:1:1:1	500	495	500	494	500	505	500	495
1:1:1:1	400	397	400	405	400	400	400	405
1:1:1:1	200	202.5	200	205	200	203	200	200
	200	198	200	197	200	198	200	203
1:1:1:1	100	97.5	100	100.9	100	101	100	100.5
	100	99.0	100	98.0	100	100	100	101.0
1:1:1:1	50	48.7	50	47.5	50	45.9	50	49.0
	50	48.9	50	51.3	50	49.0	50	51.8
1:1:1:1	20	19.2	20	19.7	20	18.7	20	21.5
10:1:1:1	1000	—	100	98.4	100	101	100	99.0
	1000	—	100	101	100	98.2	100	98.5
50:1:1:1	4000	—	80	80.5	80	79.3	80	80.0
	4000	—	80	81.0	80	79.0	80	83.0
100:1:1:1	4000	—	40	41.9	40	37.5	40	41.0
	4000	—	40	43.0	40	37.8	40	38.0

*Eriochrome Black T.* A procedure exactly analogous to that described for the indirect estimation of lead with Eriochrome Black T was carried out. Beer's law was obeyed over the range 0–5 μg of cadmium/ml, and the slope of the calibration graph was 0.195 optical density units per μg of cadmium per ml at 520 mμ.

#### Blank chromatograms

The chromatographic solvent removes small quantities of iron and other metals from the filter paper, and it is necessary to apply a blank correction to values obtained for heavy-metal samples<sup>23</sup>. A procedure exactly similar to that employed in ref.<sup>23</sup> was used, and quantitative recovery was always obtained when this correction was applied. The application of an empirical correction factor such as suggested by EBEL<sup>40</sup> is not required.

#### Analysis of synthetic mixtures

Synthetic binary and ternary heavy-metal mixtures were prepared from solutions of the metal nitrates standardised gravimetrically. The separation of zinc(II), copper(II), iron(III) and bismuth(III) from lead was found to be independent of the amount of lead and the metals may be estimated to within ± 3% for amounts greater than 30 g. Binary mixtures containing lead as the major element together with zinc(II), iron(III), copper(II), or bismuth(III) containing up to 500 parts of lead to 1 part of the "trace metal" have been analysed to within ± 4% for the "trace metal".

TABLE III  
SEPARATION OF LEAD, ZINC, COPPER AND BISMUTH

Ratio Pb: Zn: Cu: Bi	Lead		Zinc		Copper		Bismuth	
	present µg	found µg	present µg	found µg	present µg	found µg	present µg	found µg
1:1:1:1	200	203.5	200	207	200	202	200	195
	200	198	200	205	200	198	200	195
1:1:1:1	100	100	100	100	100	101	100	97.5
	100	99	100	103	100	100	100	97.5
	100	100.3	100	102	100	101	100	100
1:1:1:1	50	48.0	50	49.8	50	51.2	50	48.7
	50	50.5	50	53.1	50	48.8	50	48.7
1:1:1:1	20	18.8	20	19.6	20	18.8	20	20.3*
	20	19.8	20	19.2	20	19.7	20	19.4*
10:1:1:1	1000	—	100	97.3	100	98.0	100	99*
	1000	—	100	98.6	100	98.5	100	99*
50:1:1:1	4000	—	80	82.0	80	78.8	80	79.5*
	4000	—	80	81.3	80	79.6	80	78.8*
	2000	—	40	40.8	40	39.4	40	39.3*
	2000	—	40	40.5	40	39.0	40	39.4*
100:1:1:1	4000	—	40	41.3	40	39.0	40	40.2*
	4000	—	40	42.0	40	38.7	40	40.1*

\* After acid washing, the paper was eluted with solvent to reduce heavy metal impurities.

TABLE IV  
SEPARATION OF LEAD, CADMIUM, COPPER, ZINC, BISMUTH AND MERCURY\*

Ratio Pb: Cd: Cu: Zn: Bi: Hg	Lead		Cadmium		Copper		Zinc		Bismuth	
	present µg	found µg	present µg	found µg	present µg	found µg	present µg	found µg	present µg	found µg
1:1:1:1:1:1	200	203.7	200	205	200	203	200	207	200	193
	200	198	200	205	200	201	200	205	200	194
	100	96	100	96	100	99	100	104	100	97
50:1:1:1:1	4000	—	80	75	80	79	80	83	80	78

\* Mercury analyses were not carried out.

For separation of more complex mixtures reference should be made to Tables II, III and IV where the results are fully tabulated.

#### SUMMARY

By using a simple descending-elution technique, in conjunction with an anion exchange separation, it has been found possible to analyse for numerous heavy

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metals (including lead) in lead-containing synthetic mixtures. This method is of particular value for the estimation of small amounts of iron, copper, cadmium, zinc, and bismuth in lead.

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