The Determination of Lead in Potable Waters

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The presence of lead in normal human dietaries has now been established. It has been shown by Lynch *et al.*[1] (1934) and by Tompsett and Anderson[2, 3] (1935, 1936) that lead occurs in the tissues of persons with no history of exceptional exposure to lead. In such bones as the tibia and femur the concentration of lead may reach and actually exceed 100 mg. per kg. of fresh tissue. It is evident that absorption and retention of lead must occur at the low levels existing in the normal human diet. The ingestion of lead by patients in the Glasgow Royal Infirmary was found to amount to about 0·25 mg. per diem. From analyses of the excreta of three normal laboratory workers, it would appear, however, that the normal ingestion of lead may reach values of 0·5 mg. or more per diem.

At the present time, the minimum amount of lead consumed per diem that will produce symptoms of lead poisoning is not known. Thus it would appear important to preserve the level of lead in the human diet as low as possible. Of the components of the human diet, drinking water has probably most often been the direct cause of lead poisoning.

Natural waters do not, as a rule, contain lead, but during passage along lead pipes they may dissolve dangerous amounts. An accurate method for the determination of lead in potable waters is thus essential. The colorimetric sulphide method has most generally been used for this purpose, but it is agreed that this is not an ideal method.[4]

Allport and Skrimshire[5] have described a method for the determination of lead in dyestuffs, etc., in which the lead is separated from ammoniacal solutions by means of a chloroform solution of diphenylthiocarbazone, and determined by the colorimetric sulphide method. This method has been utilised by Lynch *et al.*[1] in the determination of lead in human tissues.

Fischer and Leopoldi[6] showed that diphenylthiocarbazone could be utilised for the colorimetric determination of lead, and in a recent communication Tompsett and Anderson[2] described a method for the determination of lead in excreta and tissues. In this method a preliminary separation of lead is made with sodium diethyldithiocarbamate, after which the lead is determined colorimetrically with diphenylthiocarbazone.

In an application of this method to the determination of lead in potable waters, it was found that, except in certain instances, the lead could be determined directly with diphenylthiocarbazone.

The Direct Determination of Lead in Water.—Diphenylthiocarbazone dissolves in organic solvents, such as carbon tetrachloride and chloroform, to form green solutions. It is soluble in slightly alkaline, but not in acid water. Alkaline aqueous solutions of diphenylthiocarbazone are yellowish-brown in colour. Diphenylthiocarbazone is particularly sensitive to traces of oxidants, *e.g.* nitric acid, perchloric acid, etc., by which it is converted into an oxidation

product. This product dissolves in carbon tetrachloride to form a yellow solution, but it is insoluble in water.

With many metals diphenylthiocarbazone forms complexes which dissolve in carbon tetrachloride to produce typically coloured solutions.

The following is a description of the method that has been adopted for the direct estimation of lead in water:

REAGENTS.

1. Concentrated sulphuric acid—Analytical reagent quality.
2. Perchloric acid—Analytical reagent quality.
3. Glacial acetic acid—Analytical reagent quality.
4. Ammonia sp.gr. 0·880—Analytical reagent quality.
5. Carbon tetrachloride—Analytical reagent quality.
6. Sulphurous acid, 5 per cent.—lead-free.
7. Potassium cyanide, 10 per cent.—"PbT" (B.P.). This is diluted 1 in 10 as required.
8. Sodium citrate, 20 per cent.—lead-free. A lead-free solution is prepared as follows:—To 1 litre of a 20 per cent. solution in water, 100 ml. of a 0·1 per cent. solution of diphenylthiocarbazone in chloroform are added, and the mixture is shaken vigorously and preserved in a bottle. Before use, a portion of the sodium citrate solution is shaken with a fresh 0·1 per cent. solution of diphenylthiocarbazone in chloroform. After separation, the aqueous solution is passed through a filter-paper to remove suspended particles of chloroform.
9. Diphenylthiocarbazone, a 0·1 per cent. solution in carbon tetrachloride. Commercial diphenylthiocarbazone contains a yellow oxidation product, which is soluble in carbon tetrachloride but not extracted by alkali cyanide. The commercial product is purified as follows:—One hundred ml. of a 0·1 per cent. solution in carbon tetrachloride are extracted with several 100-ml. portions of 0·5 per cent. ammonia. Diphenylthiocarbazone passes into the aqueous phase, leaving the oxidation product in the carbon tetrachloride. The ammoniacal extracts are passed through filter-paper to remove suspended particles of carbon tetrachloride, and then acidified by addition of sulphurous acid. The green precipitated diphenylthiocarbazone is extracted with 100 ml. of carbon tetrachloride. This solution, if preserved under a layer of sulphurous acid, will keep indefinitely.
10. Standard solution of lead acetate:—Lead acetate, $Pb(C_2H_3O_2)_2.3H_2O$, (0·1831 g.) is dissolved in distilled water containing 5 ml. of glacial acetic acid, and the volume is then made up to 1 litre with distilled water. One ml. of this solution is equivalent to 0·1 mg. of lead. As required, this solution is diluted so that 1 ml. is equivalent to 0·01 mg. of lead.

Water distilled in glass vessels was used throughout this work. Filter-papers were washed with dilute acid and then with distilled water. Pyrex glassware was used.

METHOD.—A volume of water containing about 0·05 to 0·10 mg. of lead is evaporated to a small volume in a 300-ml. Pyrex flask, and 1 ml. of conc. sulphuric acid and 1 ml. of perchloric acid are added. The heating is continued until

organic material is destroyed, and the excess of perchloric acid is driven off. The solution is cooled, and the following liquids are added in the order given:—Ten ml. of water, 1 ml. of glacial acetic acid, 5 ml. of 20 per cent. sodium citrate solution, and 5 ml. of ammonia (sp.gr. 0·880). The mixture is then diluted to 25 ml. with water.

At the same time a blank solution is prepared. One ml. of conc. sulphuric acid and 1 ml. of perchloric acid are heated in a Pyrex flask until the perchloric acid has been driven off. The liquid is cooled and the following are successively added:—Ten ml. of water, 1 ml. of glacial acetic acid, 5 ml. of 20 per cent. sodium citrate, and 5 ml. of ammonia (sp.gr. 0·880). The mixture is then diluted to 25 ml. with water.

Lead is then determined colorimetrically as follows:—Three 50-ml. glass-stoppered volumetric flasks are taken. Five to 10 ml. of the diluted digest are measured into one of the flasks, and similar amounts of blank digest are measured into the other two. Into one of the blank flasks 1 to 2 ml. of standard lead acetate solution ($\equiv$0·01 to 0·02 mg. Pb) are measured. To each flask are now added 6 drops of 5 per cent. sulphurous acid, followed by 5 ml. of potassium cyanide solution, 10 ml. of carbon tetrachloride, and 0·5 ml. of 0·1 per cent. diphenylthiocarbazone solution. After vigorous shaking the contents of each flask are poured into test-tubes. The carbon tetrachloride layer then contains the pink lead complex and also unchanged diphenylthiocarbazone. The aqueous layer also contains unchanged diphenylthiocarbazone; it should be coloured brown, indicating that excess of reagent has been used.

The aqueous layers are removed with a teat pipette. On shaking the carbon tetrachloride extracts with potassium cyanide solution, unchanged diphenylthiocarbazone passes into the aqueous phase, leaving the pink lead complex in the carbon tetrachloride. The carbon tetrachloride extracts are shaken with several 5-ml. portions of potassium cyanide solution until all the unchanged diphenylthiocarbazone has been removed, that is, until the aqueous layers are colourless; usually three or four extractions are necessary. The pink carbon tetrachloride extracts are washed once with water, and the standard and the unknown are then compared in a colorimeter.

Under these conditions the depth of colour is proportional to the quantity of lead within the range 0·01 to 0·07 mg. of Pb. When the quantity of lead is greater than 0·07 mg., the depth of colour is not proportional to the quantity. The best depth of colour for colorimetric comparison appears to be in the region 0·01 to 0·03 mg. of Pb.

In the event of 5 ml. of diluted digest containing more than 0·03 mg. of lead, a smaller volume should be taken. This should be diluted to 5 ml. with the blank solution.

By performing a complete blank, contamination can be controlled. In my experiments the blanks showed only very faint pink tinges. These were too faint to permit of colorimetric comparison. That the blanks showed a reaction at all indicates the extreme sensitivity of the test.

In preliminary experiments it was found that the carbon tetrachloride extracts invariably had yellow tints, making colorimetry difficult. This was due to

the presence of traces of perchloric acid, which produced a small amount of the oxidation product of diphenylthiocarbazone. This oxidation product is soluble in carbon tetrachloride and is not extracted by potassium cyanide solution. Its formation is prevented by the addition of sulphurous acid.

The process is specific for lead. With the exception of bismuth and stannous tin, other metals do not form complexes with diphenylthiocarbazone in the presence of cyanide. Bismuth and stannous tin are not likely to occur in drinking waters, but even when present, if not in too high a concentration, they do not interfere with the colorimetric estimation of lead. Bismuth forms in the presence of cyanide an orange-coloured complex with diphenylthiocarbazone. When a carbon tetrachloride extract containing the bismuth complex is extracted repeatedly with cyanide solution, the complex passes into the aqueous phase. In an actual experiment it was found that 0·02 mg. of lead could be determined in the presence of 0·1 mg. of bismuth, the bismuth complex being completely removed at the fifth extraction with cyanide. Stannous tin, which forms a crimson-red complex, behaves similarly to bismuth. In an actual experiment it was found that 0·02 mg. of lead could be determined in the presence of 0·1 mg. of stannous tin, the stannous complex being completely removed at the fifth extraction with cyanide.

The pink colours of the lead complex are quite stable in diffused light, but change rapidly to yellowish shades in bright sunlight. This appears to have a physical explanation: carbon tetrachloride is decomposed by short-wave ultra-violet light into C_2Cl_6 and chlorine, but is unaffected by long-wave ultra-violet light (McKenzie and King[7]). Any production of chlorine would undoubtedly lead to the formation of the yellow oxidation product of diphenylthiocarbazone. Short-wave ultra-violet light is present in bright sunlight, but not in diffused light.

The method was tested by determining the lead-contents of water to which known amounts of lead had been added. The water used was that supplied to the Glasgow Royal Infirmary. This is a soft water, the mineral-content of which is extremely small.

The experiments were repeated with an artificially prepared hard water. This water had the following composition:—acid potassium phosphate, 0·15 g.; calcium chloride, 0·15 g.; magnesium sulphate, 0·15 g. per litre of tap water (Glasgow Royal Infirmary).

The results are shown in Table I (p. 595).

The Separation of Lead.—Sodium diethyldithiocarbamate is particularly suitable for this purpose. This substance forms with a large number of metals complexes soluble in organic solvents.

With lead, sodium diethyldithiocarbamate forms a complex which is extracted by organic solvents to form colourless solutions. It is particularly soluble in ether. The reaction is independent of *p*H and is unaffected by the presence of citrates and pyrophosphates. The lead complex is very insoluble in water. A perceptible turbidity was observed when sodium diethyldithiocarbamate was added to 0·05 mg. of lead in 100 ml. aqueous solution.

With iron, sodium diethyldithiocarbamate forms a complex which is extracted by organic solvents to produce dirty brown solutions. The iron complex,

however, is not formed in the presence of pyrophosphate when the *p*H exceeds 7·5, or in the presence of citrates when the *p*H exceeds 9.

As a reagent for the separation of lead, sodium diethyldithiocarbamate has distinct advantages. It is a very stable substance, and is unaffected by traces of oxidants. To prevent the extraction of iron the separation may be carried out, (i) in the presence of pyrophosphate, the *p*H exceeding 7·5; or (ii) in the presence of citrate, the *p*H exceeding 9.

TABLE I

A. Tap water (Glasgow Royal Infirmary).
Initial lead content:—0·02 mg. Pb per litre.

	Lead added, per litre mg.	Total lead found, per litre mg.
1	0·125	0·135
2	0·125	0·145
3	0·250	0·295
4	0·500	0·525
5	0·500	0·525

B. Artificially prepared hard tap water.
Initial lead content:—0·03 mg. Pb per litre.

	Lead added, per litre mg.	Total lead found, per litre mg.
6	0·125	0·145
7	0·250	0·285
8	0·500	0·535
9	0·500	0·525

The second procedure is applicable to solutions in which the concentrations of phosphates of the alkaline earths, iron, etc., are low. For solutions in which the concentrations of phosphates of the alkaline earths, iron, etc., are high, the first procedure must be used. The solutions should then, in addition, contain citrate, which is necessary to prevent the precipitation of phosphates.

The second procedure is applicable to drinking waters, owing to their comparatively low content of phosphates, iron, etc. The process does not effect a specific separation of lead, as certain other metals (*e.g.* copper, bismuth, nickel, cobalt, etc.), if present, will be extracted. None of the extracted metals interferes with the colorimetric estimation of lead with diphenylthiocarbazone. The method effects the separation of lead from iron, which is all that is required.

A volume of the water containing about 0·05 to 0·10 mg. of lead was evaporated to a small volume in a 300-ml. Pyrex flask. Then 1 ml. of conc. sulphuric acid and 1 ml. of perchloric acid were added, and the heating was continued until the organic matter was destroyed and excess of perchloric acid driven off.

The liquid was cooled, and the following were added in the order named:—Twenty ml. of water, 1 ml. of glacial acetic acid, 5 ml. of 20 per cent. sodium citrate solution, and 5 ml. of ammonia (sp.gr. 0·880). The mixture was then transferred to a separating funnel, the volume, after the addition of washings,

amounting to 30 to 40 ml. Care was taken that the reaction of the fluid exceeded *p*H 9.

Two ml. of a 2 per cent. solution of sodium diethyldithiocarbamate in water were added, followed by 25 ml. of ether, the mixture was shaken vigorously, and, after separation, the aqueous layer was run off. The ethereal extract was washed with 10 ml. of water and then run into a 300-ml. Pyrex flask, and the separating funnel was washed out with a further 5-ml. of ether. The extraction process with ether was repeated and carried out 3 times in all.

The ether was evaporated from the combined extracts, and the residue was heated with 1 ml. of conc. sulphuric acid and 1 ml. of perchloric acid until organic matter was destroyed and excess of perchloric acid driven off.

After cooling, the following in order were added:—10 ml. of water, 1 ml. of glacial acetic acid, and 5 ml. of ammonia (sp.gr. 0·880). The mixture was then diluted to 25 ml. with water, and lead was determined colorimetrically with diphenylthiocarbazone, as described. Complete blank tests were carried out.

The method was tested by determining the lead-contents of waters to which known amounts of lead had been added. The water used was that supplied to the Glasgow Royal Infirmary.

The experiments were repeated with an artificially prepared hard water containing iron. This water had the following composition:—acid potassium phosphate, 0·15 g.; calcium chloride, 0·15 g.; magnesium sulphate, 0·15 g.; iron alum, 0·1 g. per litre of tap water (Glasgow Royal Infirmary).

The results are shown in Table II.

TABLE II

A. Tap water (Glasgow Royal Infirmary).
Initial lead content:—0·02 mg. Pb per litre.

	Lead added, per litre mg.	Total lead found, per litre mg.
1	0·050	0·065
2	0·250	0·280
3	0·500	0·515
4	0·750	0·755

B. Artificially prepared hard tap water containing iron.
Initial lead content:—0·03 mg. Pb. per litre.

	Lead added, per litre mg.	Total lead found, per litre mg.
5	0·100	0·115
6	0·200	0·220
7	0·400	0·445
8	0·500	0·513

SUMMARY.—The lead-content of potable waters may be estimated colorimetrically with diphenylthiocarbazone.

Provided the iron-content is not too high, the reaction may be applied directly.

When the iron-content is high, a preliminary separation of the lead is necessary. Sodium diethyldithiocarbamate is a suitable reagent for this purpose.

References

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