

Determination of Thallium in Biological Material by Flame Spectrophotometry and Atomic Absorption

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Flame-spectrophotometric and atomic-absorption methods of assaying trace amounts of thallium in biological material have been investigated. With the Perkin-Elmer, Model 303, spectrophotometer atomic absorption is the more sensitive and yields detection limits comparable with those reported in the literature for the most sensitive types of flame-emission equipment. A simple and rapid method of micro sampling by using a tantalum boat is described. It enables nanogram amounts of thallium (down to 3 ng) in 50 to 100 μ l of blood and urine to be determined with an accuracy and precision of 3 to 5 per cent. This represents an increase in sensitivity of at least twenty-five times over conventional atomic-absorption spectrophotometry. The results obtained with the tantalum boat are susceptible to inter-element interferences, and calibration by using the additions method is essential for accurate quantitative results.

THIS laboratory was recently requested to carry out an extensive analysis for thallium of the body of a deceased woman suspected of having died from thallotoxicosis.¹ Poisoning resulting from the ingestion of thallium salts is rare in the British Isles, although cases of thallotoxicosis arising from therapeutic accidents with scalp preparations containing thallium(I) acetate have been reported.² In many countries, however, the highly toxic thallium(I) salts are readily obtainable in the form of rodenticides, and cases of thallium poisoning are occurring to an increasing extent.^{3,4,5} Reliable and rapid methods are therefore necessary for the quantitative determination of thallium in tissue, blood and urine for use in investigations of cause of death and for following the effect of chemotherapy in the treatment of thallium poisoning.

Many methods for determining thallium in biological material have been reported in the literature.^{6,7,8} Colorimetric and titrimetric methods are generally not sufficiently specific for reliable quantitative work,^{9,10,11,12,13} and gravimetric procedures are too insensitive for trace amounts of thallium.¹¹ Polarographic methods, although both sensitive and specific, require special equipment and techniques, and are not well suited for the occasional analysis in clinical or forensic science laboratories.

Flame-photometric methods of analysis satisfy all of the requirements, and are not only ideally suited to the occasional analysis, but are also rapid and simple enough for screening large numbers of samples should the need arise. A further advantage of flame photometry is that it can be used to determine many elements and is, therefore, of particular value in forensic science investigations. In this respect the atomic-absorption and flame-emission methods complement each other, as some elements are more sensitive to atomic-absorption and others to flame-emission techniques. For this reason many flame spectrophotometers are designed for both atomic-absorption and flame-emission measurements. Frequently flame-emission spectrophotometry is used to obtain a complete qualitative analysis, the detected elements being subsequently determined quantitatively either by flame emission or atomic absorption, depending on the sensitivities of the elements to these methods and their concentrations in the sample. Recently the development of the "sampling boat" technique of presenting samples to the spectrophotometric flame has resulted in large gains in sensitivity for elements that are readily atomised, and has eliminated much of the sample pre-treatment necessary for reliable analyses of blood and urine samples.¹⁴ This paper describes the atomic-absorption and flame-emission studies carried out in this laboratory to devise suitable procedures for the quantitative determination of thallium in body fluids and tissue.

EXPERIMENTAL

EQUIPMENT FOR FLAME PHOTOMETRY—

The atomic-absorption equipment consists of a Perkin-Elmer, Model 303, double-beam spectrophotometer. This instrument is equipped with a null read-out recorder accessory coupled to a Perkin-Elmer Hitachi 165 recorder, which includes scale expansion and a response-time accessory, thus enabling low-level trace analysis to be carried out. The standard Perkin-Elmer burner head is replaced with the 3-slot "Boling" burner^{15,16} and an air-acetylene fuel mixture used. For flame-emission studies the Model 303 spectrophotometer is converted into a single-beam instrument with the Perkin-Elmer emission accessory. This accessory incorporates a synchronous chopper for the beam produced by the emitting flame and a scan motor which, geared to the wavelength control, permits the wavelength range of interest to be scanned at eight different speeds. A diffusion total-consumption burner is frequently used by many workers with this equipment. The instrumental settings for the determination of thallium by atomic-absorption and flame-emission measurements are summarised in Table I.

TABLE I

INSTRUMENTAL DETAILS FOR THE DETERMINATION OF THALLIUM BY FLAME-EMISSION AND ATOMIC-ABSORPTION SPECTROPHOTOMETRY

| | Atomic absorption | Flame emission |
|--------------------------------|-------------------------|----------------------------------|
| Instrument | Perkin-Elmer, Model 303 | Modified Perkin-Elmer, Model 303 |
| Fuel mixture | Air - acetylene | Air - acetylene |
| Burner | Boling | Boling |
| Radiation source | Hollow-cathode lamp | None |
| Source current | 12 mA | — |
| Wavelength | 276.8 nm | 535.0 nm |
| Slit setting | 5 | 3 |
| Gain | — | 4.5 |
| Recorder input voltage | 10 mV | 2 mV |

"SAMPLING BOAT" MODIFICATIONS—

The micro-sampling boat technique of presenting samples to the flame photometer described by Kahn, Peterson and Schallis¹⁴ gives greater efficiency of sample consumption and results in substantially improved detection limits for readily atomised elements such as thallium. The boat material must be able repeatedly to sustain acetylene - oxygen flame temperatures and also have good heat conduction properties. Tantalum is one of the materials that has been used.¹⁴ In our studies we found that the tantalum boat (the width of which should be no greater than 5 mm) must be used in conjunction with the 3-slot "Boling" burner, so that a smooth gas-flow pattern is obtained around the boat. Under these conditions we have found that each tantalum boat is capable of analysing up to one hundred successive solutions before replacement becomes necessary.

For the boat method of micro sampling the Model 303 atomic-absorption spectrophotometer needs to be modified to incorporate a simple boat holder that is capable not only of moving the boat in and out of the flame but also of returning the boat to the same position in the flame for a subsequent analysis. In our equipment the boat is supported by two $\frac{1}{8}$ -inch tantalum rods which, in turn, are attached to a sliding mechanism, thus allowing the boat to be moved horizontally (Fig. 1). The position of the boat is also adjustable in the other two dimensions and, before analysis, its position when in the flame is set so that the boat lies in the centre of the spectrophotometer flame, immediately below and parallel to the sample beam of the instrument. The sampling boats (measuring 5 cm × 5 mm × 5 mm) are readily manufactured from 0.005-inch tantalum sheets with a suitably shaped steel punch. After insertion into the holder, the boat is heated in the acetylene - oxygen flame for a few minutes and the absorption of a standard thallium solution repeatedly determined, by using the micro-sampling technique, until constant readings are obtained (three or four determinations are usually sufficient). It is important to remember that the sensitivities obtained with these tantalum boats depend on their exact shape and dimensions. These will vary to a small extent from one to another and it is necessary, therefore, to calibrate each individual boat before an analysis.

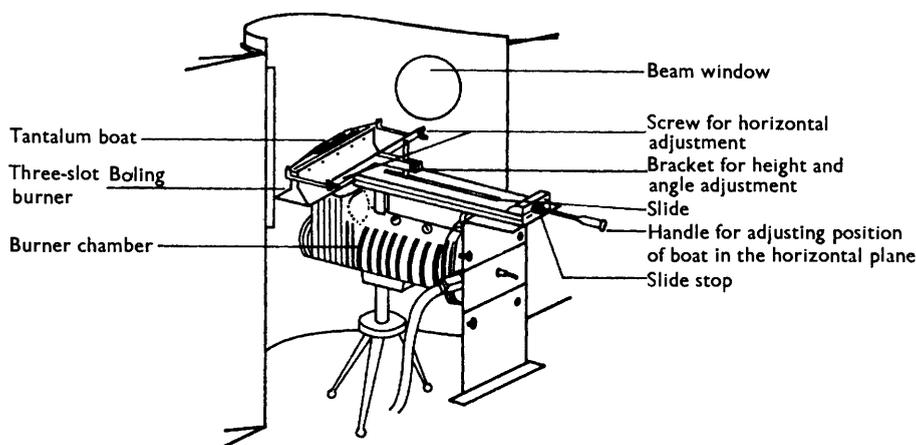


Fig. 1. Schematic diagram indicating sampling boat modifications to Model 303 atomic-absorption spectrophotometer

EXTRACTION PROCEDURES FOR FLAME-EMISSION MEASUREMENTS—

Inter-element effects frequently interfere in flame-emission analyses and, for this reason, the method of extraction used should be specific for the element under investigation. The procedures described in the literature for the extraction of thallium from tissue digest rely on the formation of thallium(III) bromide (sometimes the chloride or iodide) and the preferential removal of this compound by extraction into a suitable solvent.^{5,17,18} In many of these methods ether is used for the extraction, but we found the recovery following the addition of thallium to biological samples is poor (less than 70 per cent.) when this solvent is used. Its use would, therefore, require the standard solutions necessary for the calibration of the flame photometer to be digested and extracted in a manner identical to that for the biological sample under investigation. Other workers used hexyl methyl ketone in their extraction procedures. We obtained quantitative recovery of thallium added to tissue, blood and urine by using this solvent, but experienced some difficulty in obtaining a sufficient volume for regular use. An alternative extraction solvent frequently used in atomic-absorption spectrophotometry is isobutyl methyl ketone. The use of this solvent resulted in quantitative isolation of the thallium and no interferences were observed in subsequent flame-emission analyses. It is of interest to note that the flame-emission and atomic-absorption sensitivities recorded on aspirating hexyl methyl ketone and isobutyl methyl ketone - thallium solutions into the flame were found to be identical and superior to that obtained when diethyl ether is used as solvent. Our final extraction procedure for the determination of thallium in biological material by flame-emission spectrophotometry is a modification of the method reported by Wilson and Hausman,⁵ and is described in detail below.

METHOD—

The biological material [blood (1 ml), tissue (1 g) and stomach contents (1 g)] is accurately weighed into a 100-ml Kjeldahl digestion flask. Foodstuffs-grade concentrated nitric acid (1 ml) and foodstuffs-grade concentrated sulphuric acid (1 ml) are added and the mixture heated on a heating mantle to about 120° C. As the flask contents begin to char further portions of nitric acid are added until the digest becomes clear and all of the organic matter destroyed. After boiling off excess of nitric acid the resulting solution is allowed to cool and transferred quantitatively into a boiling tube with de-mineralised water, ensuring that the final volume is about 10 to 15 ml, including washings. A few drops of thymol blue indicator are added and the pH adjusted to between 3 and 4 by careful addition of foodstuffs-grade concentrated ammonia solution (constant cooling under a cold water tap is necessary during this operation). One drop of liquid bromine (about 50 μ l) is then added, followed immediately by 48 per cent. hydrobromic acid solution (0.5 ml); the solution is then carefully warmed over a bunsen flame to remove excess of bromine and allowed to cool to ambient temperature.

This solution is transferred quantitatively to a 50-ml separating funnel and the thallium(III) bromide extracted into the water-saturated isobutyl methyl ketone (5 ml), with shaking by hand for 2 minutes. The two immiscible phases are allowed to separate, the lower aqueous layer discarded and the organic layer washed with *N* hydrogen bromide solution (5 ml), the washings also being discarded. Finally, the isobutyl methyl ketone extract is transferred to a 25-ml vial for aspiration into the flame-emission spectrophotometer. A reagent blank is treated in a similar way.

EXTRACTION PROCEDURE FOR ATOMIC-ABSORPTION MEASUREMENTS—

Thallium can be extracted from biological material for atomic-absorption measurements by the procedure described above for flame-emission studies. However, as the atomic-absorption technique is accepted as being almost independent of inter-element effects, other extraction methods not specific for thallium can be used. The extraction procedures described by Berman¹⁹ involve chelation of thallium with sodium diethyldithiocarbamate and extraction into isobutyl methyl ketone. We found these procedures gave essentially quantitative recovery of thallium added to tissue, blood and urine, provided the pH of the biological fluids and digests is adjusted to the optimum value (Fig. 2) before extraction. These procedures are described in detail below.

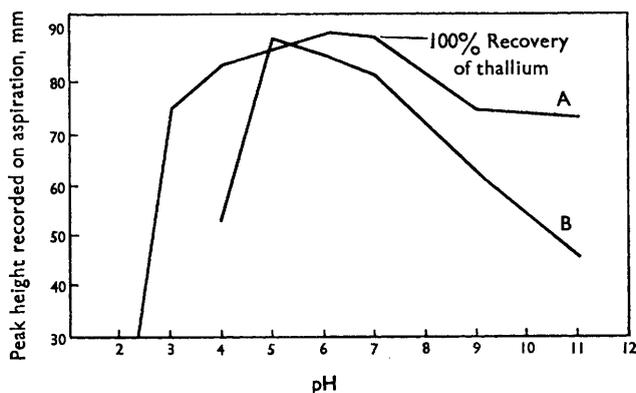


Fig. 2. Effect of pH on efficiency of extraction of thallium from urine and water. Thallium (10 μ g) extracted from 25 ml of urine and water into 5 ml of isobutyl methyl ketone by using 1 ml of 1 per cent. sodium diethyldithiocarbamate: A, urine; and B, aqueous

METHODS—

Tissue—The biological material (1 g) is accurately weighed into a Kjeldahl flask and digested in the manner described above for flame-emission studies. The pH of the resulting digest is adjusted to a value between 5 and 6 (Fig. 2) with 2.5 *N* sodium hydroxide solution, and the thallium is chelated with 1 per cent. w/v aqueous solution of sodium diethyldithiocarbamate (1 ml) and extracted into water-saturated isobutyl methyl ketone (5 ml) for determination by atomic-absorption measurements. A reagent blank is treated in a similar manner.

Blood—To whole blood (1 ml) is added an equal volume of 5 per cent. w/v trichloroacetic acid; the mixture is shaken for 1 hour and centrifuged. The supernatant liquid is then transferred to a suitable vessel and the residue washed with distilled water (5 ml), stirred and again centrifuged. The washings are decanted and added to the previous liquid. The pH of this solution is adjusted to 6 with *N* sodium hydroxide solution, 1 per cent. w/v aqueous solution of sodium diethyldithiocarbamate (0.5 ml) is added and the thallium extracted into isobutyl methyl ketone saturated with water (5 ml).

Urine—A portion of urine (2 ml) is adjusted to pH 6 by the addition of 5 per cent. w/v trichloroacetic acid or 2 *N* sodium hydroxide solution as necessary. If a precipitate is formed at this stage, the mixture is centrifuged, the supernatant liquid transferred to another vessel and the residue washed with distilled water, the washings being decanted and added to the

previous liquid, the pH of which is finally re-adjusted to 6. To the treated urine sample is added 1 per cent. w/v aqueous sodium diethyldithiocarbamate solution and the thallium chelate extracted into water-saturated isobutyl methyl ketone (2 ml) by shaking the mixture, which is centrifuged and the organic extract separated for aspiration into the flame.

Blood and urine samples can also be wet washed and the thallium extracted by using Bermans' procedure¹⁹ for tissue.

FLAME-EMISSION AND ATOMIC-ABSORPTION MEASUREMENTS—

The flame photometer is calibrated by plotting the absorption and flame-emission intensities observed for standard extracts against thallium concentration. These standard extracts are obtained from freshly prepared aqueous solutions of known concentration in the same way as the biological extracts, and are read under the same conditions and simultaneously with the samples under investigation. The resulting analytical working curves for flame emission and atomic absorption can then be used for the conversion of instrumental readings observed for unknowns into thallium concentration values. The minimum volume of an organic extract required for a reliable absorption or emission-intensity reading, by using aspiration methods of sampling, is 1 ml.

RAPID MICRO-SAMPLING TECHNIQUE FOR ATOMIC-ABSORPTION MEASUREMENTS ON BLOOD AND URINE—

Blood and urine samples (50 to 200 μ l) are introduced by pipette into the tantalum sample boat. These samples must be initially dried before analysis, otherwise spluttering occurs with resulting loss of material. This is readily achieved by bringing the sample boat to within 1 cm of the absorption flame and allowing the volatile constituents to evaporate over a period of minutes. A dried urine sample can then be inserted into the flame, the absorption peak at the thallium analytical wavelength recorded (3 to 4 seconds only are necessary) and the boat removed and allowed to cool for a subsequent analysis.

For blood analyses pre-ashing of the sample is necessary to minimise the absorption and scattering effects of carbon species produced from the organic constituents of the blood. It is important to use Noise Suppression I with its rapid electronic response for blood analyses. Under these conditions the initial absorptions associated with the carbon species (first peaks) are easily distinguished from those of thallium (second peaks) (Fig. 3).

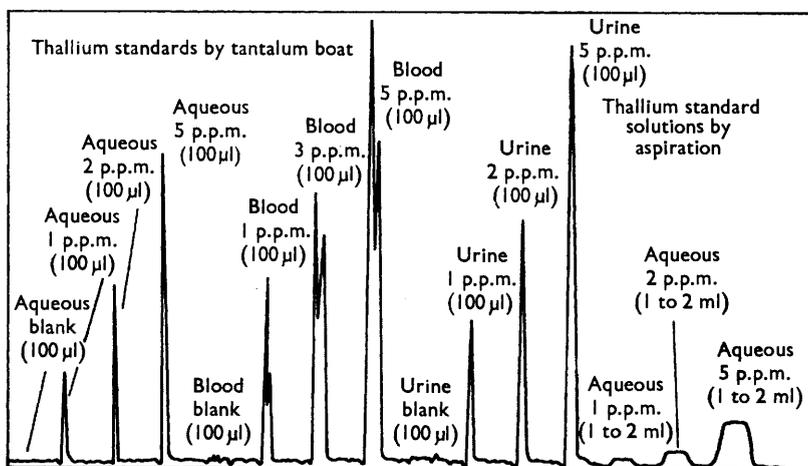


Fig. 3. Typical thallium results with tantalum boat and nebuliser. Conditions: wavelength, 276.8 nm; slit setting, 5; source current, 12mA; scale expansion, $\times 1$; noise setting, $\times 1$; and chart speed, 60 mm minute⁻¹

In our laboratory the blood sample, after initial drying, is allowed to cool; three drops of foodstuffs-grade concentrated nitric acid are then added and the boat is re-positioned 1 cm from the acetylene - oxygen flame and left in this position until no more visible smoke appears

from the sample. Finally, the boat is inserted into the flame for the analysis for thallium. In our experience the use of excessive amounts of nitric acid in the ashing procedure results in attack on the tantalum surface and is, therefore, to be avoided, as this can result in a change in the sensitivity observed with the boat. We have found that thallium-free urine and blood samples give negligible background absorptions at the thallium wavelengths with the analytical procedures described in this paper (Fig. 3).

For rapid blood analyses the spectrophotometer can be calibrated with standard aqueous solutions of thallium salts, although for the most accurate results the standard solutions must have compositions similar to the "unknowns" under investigation. However, for urine samples, the tantalum boat technique gives a substantially increased recorder response for thallium, and calibration with thallium-treated urine samples is essential.

RESULTS AND DISCUSSION

FLAME EMISSION—

The Perkin-Elmer, Model 303, atomic-absorption spectrophotometer is readily converted into a scanning single-beam flame-emission instrument, with accessories supplied by the manufacturer. By using this converted instrument we found the detection limit to be 5 p.p.m. for thallium in isobutyl methyl ketone solution. It will be apparent from this relatively high figure that the flame-emission technique lacks sensitivity with this equipment, and the scope for a full analysis for trace amounts of thallium is seriously limited. The equipment has, however, proved most useful for quantitative determination of metals present in samples at relatively high concentrations. It must also be pointed out that sensitive double-beam spectrophotometers designed for very accurate and precise flame-emission measurements are commercially available, with reported detection limits as low as 0.06 p.p.m. for thallium in aqueous solution.^{21,22} This is a substantial improvement on the detection limit of 0.2 p.p.m. we obtained for aqueous solutions by using atomic absorption, and is comparable with the figure of 0.04 p.p.m. obtained with isobutyl methyl ketone extracts, again with atomic absorption (Table II).

TABLE II
DETECTION LIMITS AND SENSITIVITIES OBTAINED FOR THALLIUM BY USING
ATOMIC-ABSORPTION SPECTROPHOTOMETRY

| | Aspiration method | | Tantalum boat technique | |
|---|---------------------|------------------------|-------------------------|------------|
| | Water | Isobutyl methyl ketone | Water | Urine |
| Solvent medium | | | | |
| Minimum volume required for a reliable analysis | 1 ml | 1 ml | 50 μ l | 50 μ l |
| Detection limits | 0.2 p.p.m. (200 ng) | 0.04 p.p.m. (40 ng) | <2 ng | <1 ng |
| Sensitivity* | 0.8 p.p.m. (800 ng) | 0.15 p.p.m. (150 ng) | 6 ng | 3 ng |

* Sensitivity defined as the concentration (p.p.m.) or weight of the element required to give a 1 per cent. change in absorption.

ATOMIC ABSORPTION—

In both atomic-absorption and flame-emission techniques the "unknown" solution is normally aspirated into the gas stream or flame and reduced to fine droplets. The solvent then evaporates, and the dry salts formed subsequently break down to form free gaseous atoms. The use of suitable organic solvents, instead of aqueous media, increases the rate of aspiration of the sample, leads to the formation of finer aerosol droplets, produces greater vaporisation in the flame and results in a reduction in flame temperature.²³ All of these factors increase the sensitivity of atomic-absorption measurements. Our previous studies on the determination of lead and cadmium in tissue and body fluids indicated that isobutyl methyl ketone is the most suitable solvent for the determination of heavy metals by atomic-absorption spectrophotometry.²⁴ The sensitivities and detection limits obtained for thallium with water and isobutyl methyl ketone as solvent are listed in Table II. The results of recovery experiments (Tables III and IV) indicate that atomic-absorption methods of analysis coupled with the extraction procedures described in this paper offer precise and accurate methods of assaying small amounts of thallium in biological material.

TABLE III

RECOVERIES OF THALLIUM ADDED TO TISSUE, BLOOD AND URINE BY CONVENTIONAL ATOMIC-ABSORPTION SPECTROPHOTOMETRY

| Thallium added to 2 g of tissue, μg | Modified Wilson and Hausman procedure | | Berman's procedure | |
|--|---------------------------------------|---------------------|-------------------------------|---------------------|
| | Thallium found, μg | Recovery, per cent. | Thallium found, μg | Recovery, per cent. |
| Tissue— | | | | |
| 2 | 2.1 | 105 | 2.00 | 100 |
| 10 | 9.8 | 98 | 10.2 | 102 |
| 25 | 24.6 | 98 | 24.3 | 97 |

| Thallium added to 2 ml of blood or urine, μg | Berman's procedure | | | |
|---|-------------------------------|---------------------|-------------------------------|---------------------|
| | Blood | | Urine | |
| Blood and urine— | Thallium found, μg | Recovery, per cent. | Thallium found, μg | Recovery, per cent. |
| 2 | 1.9 | 95 | 1.95 | 97 |
| 10 | 10.1 | 101 | 9.7 | 97 |
| 25 | 24.8 | 99 | 25.8 | 103 |

TABLE IV

REPLICATE DETERMINATIONS OF THALLIUM IN AQUEOUS, URINE AND BLOOD MEDIA BY USING ATOMIC-ABSORPTION TECHNIQUES

*Tantalum boat—*In each instance 1 μg of thallium was taken, *i.e.*, 100 μl of 1 p.p.m. standards

| Determination | Thallium determined, μg | | |
|--------------------------|------------------------------------|-------|-------|
| | Aqueous | Urine | Blood |
| 1 | 1.000 | 1.019 | 1.001 |
| 2 | 1.020 | 1.000 | 1.051 |
| 3 | 1.000 | 1.000 | 1.089 |
| 4 | 1.000 | 0.973 | 1.001 |
| 5 | 1.017 | 0.957 | 1.064 |
| 6 | 0.983 | 1.035 | 1.001 |
| 7 | 1.021 | 0.927 | 0.951 |
| 8 | 1.000 | 0.927 | 0.926 |
| 9 | 1.019 | 0.957 | 1.026 |
| 10 | 0.990 | 0.942 | 0.976 |
| Mean | 1.004 | 0.974 | 1.008 |
| Coefficient of variation | 1.6 | 3.7 | 5.1 |

*Aspiration—*In each instance 10 μg of thallium were taken, *i.e.*, 1 ml of 1 p.p.m. standards

| Determination | Thallium determined, μg | | |
|--------------------------|------------------------------------|---|---|
| | Aqueous | Urine (Berman's method ¹⁹) | Blood (Berman's method ¹⁹) |
| 1 | 9.98 | 10.37 | 9.47 |
| 2 | 10.63 | 10.37 | 11.59 |
| 3 | 10.52 | 10.52 | 10.53 |
| 4 | 9.76 | 11.23 | 11.77 |
| 5 | 10.19 | 10.99 | 11.95 |
| 6 | 10.52 | 10.37 | 11.59 |
| 7 | 9.76 | 10.99 | 11.97 |
| 8 | 10.19 | 10.29 | 11.93 |
| 9 | 9.76 | 10.44 | 11.94 |
| 10 | 9.76 | 11.32 | 10.53 |
| Mean | 10.11 | 10.69 | 11.33 |
| Coefficient of variation | 3.5 | 3.9 | 8.5 |

ATOMIC ABSORPTION WITH THE TANTALUM-BOAT SAMPLING TECHNIQUE—

The advantages of the new tantalum-boat technique are derived from its extreme simplicity and ability to analyse small volumes of biological fluids by consuming the entire sample in a very short time to give a long, narrow absorption peak for the element of interest.

This greatly improves the detection limits and sensitivities that can be obtained by atomic-absorption spectrophotometry for elements that are readily atomised. For thallium, an improvement of more than twenty-five times over the conventional aspiration technique is obtained with the boat (Table II). Similar degrees of improvement over the conventional atomic-absorption technique have been obtained with the boat for the determination of lead and cadmium in urine and blood.²⁵ Because of these increases in sensitivity the sample volumes required for analysis are drastically reduced, and the boat method of sampling is ideally suited for handling very small samples. It can be seen from the results in Table IV that the analytical precision for the determination of thallium in urine and blood compares favourably with that obtained by conventional extraction and aspiration techniques, even although a much smaller sample is required. Larger volumes of very dilute thallium solutions can be analysed if the boat is successively loaded and dried several times before analysis by insertion into the flame. A further advantage of the technique is that pre-treatment of blood and urine samples is virtually eliminated and analytical determinations are rapid.

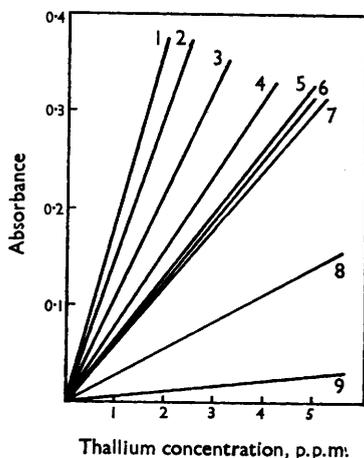


Fig. 4. Atomic-absorption calibration graphs for thallium in various media. With tantalum boat (100- μ l aliquots): 1, urine; 2, aqueous sodium chloride solution*; 3, aqueous potassium chloride solution*; 4, aqueous calcium chloride solution*; 5, blood; 6, aqueous; and 7, aqueous magnesium nitrate solution.* With nebuliser: 8, isobutyl methyl ketone solution; and 9, aqueous

*Concentration values taken from Geigy tables²⁰ (based on Na 0.4, K 0.25, Ca 0.02 and Mg 0.01 g per 100 ml of urine)

In contrast to conventional atomic-absorption techniques necessitating extraction and concentration procedures, we have found that the results obtained with the boat are susceptible to interferences. For this reason it is necessary to calibrate the equipment by using standard solutions of similar composition to the sample under investigation. With blood samples these interferences appear to be small. On the other hand for urine, interference from other constituents in the sample results in a substantial enhancement of the recorded thallium absorption (Figs. 3 and 4). A preliminary study of this phenomenon indicated that sodium, potassium and calcium in aqueous thallium solutions (Fig. 4) enhance the thallium absorption and that heavy metals (*e.g.*, lead and cadmium), phosphate and organic constituents, *e.g.*, urea, have little or no effect. Aqueous solutions of calcium and alkali metals do not absorb at 276.8 nm in the absence of thallium and the effect cannot, therefore, be caused by background absorptions or light-scattering effects but must result from the influence of

these metals on the kinetic and thermodynamic factors that control the sensitivity of the analytical determinations. The loss of energy of excitation through collision with other atoms or molecules would effectively increase the population of thallium atoms in the ground state at any given time. These quenched thallium atoms would then be able to re-absorb further photons of light of the analytical wavelength. However, this type of interference is thought to be of little significance in the absorption process. The observed effects are more likely to be explained as depressions in ionisation that would also lead to an increase in the number of thallium atoms in the ground state. In this event the introduction of readily ionised elements, such as sodium and potassium, into the flame causes the equilibrium to be shifted in favour of the formation of neutral thallium atoms and thus increases the absorption being measured. This type of interference has been observed repeatedly in the determination of calcium and potassium in the presence of excess of sodium with conventional atomic-absorption techniques.^{26,27,28} This effect does not increase proportionally with the concentration of the interfering cations but shows a plateau region (Fig. 5); sometimes a convenient addition of the interfering alkali metal can equalise sample solutions and standards. However, for samples such as urine, in which several interfering species are present, it is advisable to evaluate results by using the additions method.²⁹

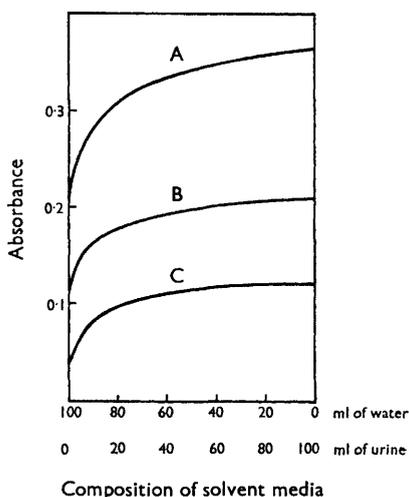


Fig. 5. Variation of interference effects with concentration of salts found in urine: A, 2.0 p.p.m. thallium standard, B, 1.0 p.p.m. thallium standard; and C, 0.5 p.p.m. thallium standard

CONCLUSIONS

The sensitivity of atomic-absorption measurements surpasses that of flame emission with the Model 225 instrument and yields detection limits comparable with those reported in the literature for the most sensitive types of flame-emission spectrophotometers.

Atomic-absorption spectrophotometry provides rapid, precise and accurate methods of assaying trace levels of thallium in biological samples.

The use of the tantalum boat method of micro sampling for atomic-absorption analyses of biological fluids offers the following advantages.

Sample pre-treatment is minimised and quantitative analysis is rapid. The technique is, therefore, ideally suited for screening large numbers of samples for toxic elements such as thallium, lead, mercury and cadmium.

Very small samples of blood and urine (50 to 200 μ l) can be analysed without loss of precision and accuracy. The boat technique has made it possible to determine "normal" lead concentrations on very small volumes of blood (100 μ l), *i.e.*, amounts easily obtained by finger puncture.²⁵

The sensitivity of the atomic-absorption method is increased by a factor of twenty-five times for thallium over aspiration methods. Similar increases in sensitivity have also been observed in this laboratory for lead and cadmium.²⁵

In contrast to conventional atomic-absorption analytical methods for blood and urine, the tantalum boat method is susceptible to inter-element interference effects and calibration must be carried out by using the method of additions.

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