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**DETERMINATION OF TRACES OF
THALLIUM IN VARIOUS MATRICES†**

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Determination of traces of thallium in various matrices

INTRODUCTION

Thallium is a relatively rare element and therefore its application is limited. The determination of traces of thallium, however, is important because of its high toxicity (maximal allowable concentration : 0.1 mg.m⁻³ in air). In addition to the availability of accurate methods for the determination of total thallium, one should consider methods for speciation (at least for the different oxidation states thallium (I) and thallium (III) and for organo halogen compounds (e.g. R₂TlBr) (1).

The determination of thallium is not an easy task as the natural contents in environmental samples are at ng.g⁻¹ levels or less. In discussing analytical methods for thallium, one should pay attention to all relevant parts of the analytical procedure : sampling, digestion, preconcentration and determination.

1. PROPERTIES OF THALLIUM AND THALLIUM COMPOUNDS

To develop and to understand analytical methods for thallium, some particular properties of the element and its compounds should be understood. Thallium (I) adsorbs onto polythene, polypropene, glass, paraffin or rubber from 0.1 M HNO₃ solutions. The adsorption depends on the treatment of the surface, ionic strength, other kinds of ions present and other quantity of thallium from solutions concentrations 1 µg.ml⁻¹ at pH 4; at pH 10 there is strong adsorption (2). In addition, some thallium compounds are somewhat volatile. Thallium (III) is easily reduced, especially at elevated temperatures. Organic thallium compounds are easily pyrolyzed into Tl(o) or Tl₂O. Table 1 presents the melting points (m.p.) and boiling points (b.p.) of some Tl(I) compounds.

Table 1. Melting points (m.p.) and boiling points (b.p.) of Tl compounds

| Compound | m.p. (°C) | b.p. (°C) |
|-------------------|-----------|-----------|
| Tl | 304 | 1457 |
| TlF | 327 | 655 |
| TlCl | 430 | 720 |
| TlBr | 315 | 480 |
| TlI | 440 | 823 |
| Tl ₂ O | 596 | 1080 |
| TlNO ₃ | 206 | 430 |

The volatility of Tl compounds as indicated by the data in Table 1, is a drawback in digestions by fusion or dry ashing. On the other hand, it facilitates separation for example in a hydrogen, oxygen or hydrochloric acid stream (3, 4, 5), from other elements which do not form volatile compounds under the same conditions.

Most Tl(I) compounds dissolve in water; $TlBr$, $TlIO_3$, Tl_2S and salts of fatty acids are slightly soluble ($0.1 - 1 \text{ g.L}^{-1}$), Tl_2CrO_4 , TlI ($0.01 - 0.1 \text{ g.L}^{-1}$) and Tl-tetraphenyl borate are Tl(III) Tl(I) $E^\circ = +1.25 \text{ V}$) and hydrolyses readily. Alkyl Tl compounds like R_2TlX and $RTlX_2$ (X is an anion) are generally more stable than the corresponding lead compounds. R_2Tl compounds hydrolyse immediately in water to the dialkyl compounds (4). Tl(I) forms strong complexes with sulphur-containing ligands (dithizone, dithiocarbamates, etc.) and with basic nitrogen-containing ligands. Weak complexes are formed with oxygen ligands, EDTA, cyanide and fluoride, so these ligands can be used to mask other ions. Tl(III) associates as tetrahalide complexes with ammonium-nitrogen, basic oxygen (ether) and phosphorus (e.g. phosphine oxides).

2. DIGESTION

Determination methods such as spectrophotometry or voltammetry require a complete digestion of organic compounds in the sample and this should be considered when selecting a digestion procedure. Because of the volatility of the element and many of its compounds, fusions in an open system are not recommended. The same holds for dry ashing at temperatures above ca. 400°C . With fuming H_2SO_4 or $HClO_4$ in an open system losses may also occur (6). For AAS (see chapter 4 for a description of the aberrations) such a complete sample decomposition is not necessary. Thus human tissues have been digested with HNO_3/H_2O_2 prior to Tl determination by AAS (7, 8).

Where higher temperatures (200°C) are required (e.g. for fat-containing biological samples, and ores) a pressurized digestion in PTFE (6) using HNO_3 , HNO_3/HF , $HClO_4/HNO_3$ or similar mixtures are recommended (4). The interference of HF in ET-AAS and ICP-AES determinations can easily be avoided by removing HF with boric acid (5).

In a closed system digestion the volatility of Tl can be used to separate it from accompanying elements. Combustion in oxygen is followed by volatilisation in a stream of hydrogen, oxygen or hydrochloric acid gas, of the metal, the oxide or the chloride, respectively, and subsequent freezing out. Only traces of a few other elements are present with the thallium after such a separation step in combination with the decomposition step (5, 9, 10). The volatilization separation step by simple fusion with $MgCl_2 \cdot 2 H_2O$ is especially useful for ores and rocks. A mixture of the sample and magnesium chloride are placed in a quartz tube, which is drawn out into a long capillary tube at the top end. The tube is put into a furnace with the capillary protruding outside. On heating, HCl is formed which transports Tl and $TlCl$ into the cold part of the capillary where the Tl compounds are trapped (10). A more rapid system involves fusion in a boat placed into a stream of O_2 or H_2 in a quartz apparatus. The gas stream transports the Tl-compounds formed into a cold trap (5,9).

Biotic samples may be mixed with $MgCl_2$ (in water-free form) and combusted in an oxygen stream in a special quartz device (Trace-O-Mat^(R)). Tl is trapped quantitatively in a cold trap (liquid nitrogen). Samples which are not easily combustible are first mixed with cellulose powder before combustion (4).

3. PRECONCENTRATION METHODS

Separation of interfering elements as well as concentration of the species to be determined involves carefully selected procedures which have to be studied before application to an unknown matrix. Not all procedures which have been successful for a certain matrix type can be converted and transferred to another (even similar) type of matrix without checking accuracy and precision by standard addition or an independent method.

Where small quantities (ng.g^{-1} range) are involved, separation and concentration processes should be combined to reduce systematic errors (12). Some examples of separation methods include :

- 1) Coprecipitation (table 2). This is not selective, but the high concentration factor and the fact that one gets a new uniform matrix make the method attractive for some purposes;
- 2) Anodic electrolysis of Tl (Table 3) is an excellent separation method. However, the method requires special equipment and needs 1 hour's operation time;
- 3) Ion exchange (Table 4) allows a large concentration factor and yields interference-free solutions, but the method is also time-consuming.
- 4) Liquid-liquid extraction (Table 5) is a fast method and can easily be checked; the method has a relatively small concentration factor.

4. METHODS OF FINAL DETERMINAL

In order to avoid elemental cross-interferences, small amounts or low concentrations should be determined after an appropriate separation of Tl from the matrix and other elements. The preconcentrated or separated Tl can be determined with most of the common techniques of trace analysis.

Table 2 Separation and concentration by coprecipitation

| Collector | Sample solution | Separation from | No separation from | Reference |
|-------------------------------------|--|-----------------------------------|--------------------------------------|-----------|
| AgCl | pH 4-5; EDTA | most elements | - | 11 |
| Hg ₂ Cl ₂ | pH > 2.5 | Ba, Sr, Mg, Fe | Au, Ag, Pb, Se, Te, As, I, Sn, Sb | 2 |
| AgI | pH 10; acetate/citrate | Sb, Au, Cr, Cu, Hg | - | 2 |
| AgI+ 1,10-phenanthroline | pH 3.5 - 4.5 | Mn (matrix) | - | 13 |
| Pb I ₂ | pH 4.5; acetate, sulphite, NH ₂ OH | many elements | - | 2 |
| Mg(OH) ₂ | natural waters; Br ₂ | Ti, V, Ni, Cr, Pb, Cu, In, Cd | - | 2 |
| Al(OH) ₃ | acidified; KBrO ₃ | | | 14 |
| Fe(OH) ₃ | conc. salt solutions | salt matrix (K, NH ₄) | - | 2 |
| Fe(OH) ₃ | pH 4.6; acetate | Cd (matrix) Ag, Hg | Al, Ga, In, Bi | 15 |
| Fe(OH) ₃ | 2M HCl/Br ₂ + pH 4.6 | | | 2 |
| MnO ₂ .aq. | acidif; Br ₂ | Pb (matrix) | Sn, As | 9 |
| MnO ₂ .aq. | HNO ₃ ; Br ₂ | | | 2 |
| MnO ₂ .aq. | H ₂ SO ₄ ; H ₂ O ₂ | salt matrix (K, NH ₄) | - | 2 |
| Zr(OH) ₄ | conc. salt solutions | | Cd, Co, Fe, In, Mn | 2 |
| CuS | 3M HCl | | Ni, Pb, Zn, Pd, Ir Pt, Rh | 16 |
| | | Ga, Sb | | |
| Bi ₂ S ₃ +TPB | EDTA; pH 5-6 | | As, Sb | 2 |
| CdS | pH 2,5; ascorbic acid | Au, Si, Na, Al | - | 2 |
| PbCrO ₄ | 0.02 M HNO ₃ | Fe, Si, Mg, Ca, Al | Au, Sb, Mo, W | 17 |
| Methyl orange | 0.2 M HCl; Br ₂ | Al | Bi, Cd, Co, Fe, In | 2 |
| APDC | | | Ni, Pb, Zn | 18 |

Table 3 Electrolytic Tl preconcentration

| Sample matrix | Electrode | Working condition | References |
|---------------------------------|---------------------------------|--|------------|
| Aqueous solution | cathodic; rotating copper disc. | 6 V | 19 |
| Natural waters | platinum spiral | - 1.0 V (vs Ag/Ag Cl) | 20 |
| Na ₃ PO ₄ | graphite disc | 15 V | 2 |
| Ga, GaAs | carbon tip | - 0.8 V (vs H ⁺ /H ₂) | 2 |
| Cd | Zn powder | currentless | 2 |
| NH ₄ NO ₃ | anodic; Pt basket | 2 A; 1 h | 2 |
| Glass | | 20 mA; 2 V | 21 |

Table 4 Some methods of separation and concentration by use of organic ion exchangers

| Type of exchanger | Sample solution | Tl oxidation state | Separation from | References |
|-------------------|--|--------------------|-----------------------------|------------|
| cation | tartrate pH 3-5 | I | Zn, Sn, Cd, Al, Fe, Sb | 2 |
| | EDTA pH 4 | I | Hg, Bi, Cu, Fe, Pb, Zn | 2 |
| | 0.1 M HCl/Cl ₂ ; 50% acetone | III | Al, Ca, In | 2 |
| | 0.1 M HCl/Cl ₂ | III | Matrix (e.g. rock, soil) | 22 |
| anion | 0.1 M HCl/Br ₂ | III | sea water | 2 |
| | 2 M HCl | I, III | Zn, Pb, Cd | 2 |
| | > 0.5 M HBr | III | "specific" | 2 |
| | 2 M HCl or 0.1 M HCl/Br ₂ | III | sea water | 23 |
| | 6 M HCl | III | Mn, Mo, V | 24 |
| | 0.1 M HCl/Br ₂ | III | Pb | 2 |
| (Active charcoal) | 0.15 M HBr/BF ₃ | III | "specific" | 25 |
| | pH 8; DDTC; borate | I | "specific" | 26 |

Table 5 Some liquid-liquid extraction methods

| Reagent | Aq. phase | Organic phase | Separation from | No separation from | Ref. |
|-------------------------|---|---|----------------------------------|-----------------------------------|------|
| - | 6.7 M HCl | MIBK; AAc; DPE; AA | In (matrix) | - | 27 |
| - | HCl/Br ₂ | DPE | Pb (matrix) | - | 28 |
| - | HBr | DE | - | - | 29 |
| - | 0.1 M HBr/Br ₂ | DPE | - | Au | 30 |
| - | 0.5 M HBr/Ce(IV) | DPE | most elements | - | 31 |
| Mesityloxiide | 1-3 M HCl | toluene | - | Sb, Sn, V, Hg | 32 |
| TTA | pH 4.4; Br ₂ | benzene | Sr, Zr, actinides | - | 33 |
| 8-mercapto quinoline | variable | CHCl ₃ | Fe, Co, Cu, Pd, Zn, Mo, V, Sb | Ni, Mn | 2 |
| TBM | pH > 11; KCN/NH ₂ OH | benzene | - | - | 35 |
| DDTC | pH 10.5; KCN/ citrate/asc.acid | MIBK | - | - | 36 |
| HMA-HMDC | pH 2-3; formate/citrate | DIPK + xylene | Fe (matrix) | Ag, Bi, Cd, Co, Pb, Ni, Cu | 37 |
| Dithizone | 3M NaOH/ tartrate/citrate | CCl ₄ | - | Cd, Cu, Hg | 2 |
| Dithizone | pH 11; cyanide/ citrate | CHCl ₃ | - | Hg | 38 |
| K-Xanthates | pH 8; citrate/ tartrate | MIBK | - | Bi | 2 |
| TOA | 2M-H ₂ SO ₄ /1 M KI | xylene, MIBK | Fe (matrix) | - | 2 |
| TOPO | HCl KI | MIBK | Ni, Fe, Al | Sb, Bi, Pb, Sn, Cd, Cu, In, Zn | 2 |
| Cyclopenta- diene | 2M KOH/KCN | CH ₂ Cl ₂ /CHCl ₃ ; benzene; MIBK | - | - | 39 |

This section deals with these techniques, such as u.v.-visible spectrophotometry, FAAS, GF-AAS, emission spectrometry after excitation by ICP, CMP, MIP, arc or spark and voltammetric techniques, esp. DPASV.

Tl(I)-ion sensitive electrodes (ISE) are not sufficiently sensitive or selective in the presence of the large amount of alkali metal ions which are usually present. The detection power of the usual XRF-techniques is not sufficient for the ng.g⁻¹ level. Methods such as TXRF (total reflectance excitation XRF) or excitation with charged particles (PIXE) are not yet sufficiently developed for determinations of Tl in real samples. Photon activation (17) and other radiochemical methods (e.g. radiochemical isotope dilution (28), although sufficiently sensitive) have seldom been used.

Atomic fluorescence spectrometry (AFS) and MS have not been applied frequently for routine problems. Isotope dilution mass spectrometry, however, is a promising method for the ng.g⁻¹ range with a good precision and accuracy if used properly (80, 81, 82, 83).

4.1. Spectrophotometry

Table 6 presents a summary of spectrophotometric Tl-determinations using chelates and ion pairs. This method is relatively simple; especially in combination with liquid-liquid extraction₂₁ and is sufficiently sensitive to allow determinations down to 50 ng.mL⁻¹ (31). The method using the (TlBr₄)⁻-Rhodamine B₁ ion pair has been carefully investigated (34). Levels as low as 10 ng.mL⁻¹ Tl can be determined in the presence of all elements which are commonly found in environmental matrices (e.g. waters, air, dust, soils, plants, animal tissues etc.).

4.2. Flame atomic absorption spectrometry (FAAS)

At the µg.mL⁻¹ level and higher, FAAS is a reliable method for final determination (41). Using the solution injection (42, 43) or noble metal loop techniques (44) the detection limit can be increased by an order of magnitude. Table 7 presents a summary of Tl-determination with FAAS.

4.3. Graphite furnace AAS (GF-AAS)

The lower limit of detection of Tl by GF-AAS is about 2 ng.mL⁻¹. The method, however, is sensitive to interferences by other elements; e.g. halides and Fe which can considerably reduce the signal. When applying GF-AAS one should consider a separation of Tl prior to the determination. Table 8 presents a selection of methods applicable to practical problems. Further applications are reviewed recently (51).

4.4. Emission spectrometry (ES)

With the classical excitation techniques (arc and spark) lower limits of detection (1 - 0.02 µg.g⁻¹ Tl) can be achieved. The technique is most sensitive when the Tl is volatilized directly from the electrode as its halide or when it condenses directly onto the electrode (9).

Table 6 Some Spectrophotometric Tl-determinations applicable at the higher ng.g⁻¹ level

| Oxidation State | Reagent | Sample solution | Extraction with | Interferences (at conc. comparable to Tl-conc.) | No interferences from | Detection limit (ng.mL ⁻¹) | Ref. |
|-------------------|---|--|--|---|-------------------------------|--|------|
| I | PAN | acetate buffer pH 4-6 | CHCl ₃ | Ga, In, Co, Ni Zn, Cu, Fe, Cd | Sb, Ti, Mo | 40 | 2 |
| | Dithizone | pH > 11; citrate/KCN | CHCl ₃ | Hg, Pb, Bi, Sn | - | - | 38 |
| | Cu-DDTC | pH = 11 | CCl ₄ | Bi | 60 cations investigated | | 40 |
| III | Brilliant green | 6 M HCl/Br ₂ * | DPE | Au, Sb | In (matrix) | 10 | 27 |
| | | HCl/Br ₂ * | toluene | Sb, detergents | Sn, As, Hg, Co, Zn, Cu | 400 | 2 |
| | | 1 M HCl/Cl ₂ * | toluene + mesityloxiide | Sn, Sn | 23 cations investigated | 50 | 32 |
| | Methyl violet | 0.3 M HCl/H ₂ O ₂ * | benzene; toluene | | Fe, Mn, Ni | 80 | 2 |
| | | 2 M H ₃ PO ₄ /Cl ₂ * | toluene | Sb, Au, Hg, I ⁻ , ClO ₄ ⁻ | | | 2 |
| | Rhodamine B | 0.5 M HBr/V (IV) | DPE | Au, I | 37 cations investigated | 10 | 34 |
| | Crystal violet | 0.1 M HBr/Br ₂ * | DPE | | Zn, Al, Cu, Mg, Fe, Pb, In | 50 | 2 |
| Meldola blue | 1 M HBr/Br ₂ * | Benzene/ acetone/chloro benzene/CHCl ₃ / CH ₂ Cl ₂ | Au | | 200 | 2 | |
| Victoria blue 4 R | 3.5 M H ₂ SO ₄ /Cl ₂ | Benzene | Au, Sb, Hg, Ir, Pt, I ⁻ , SCN ⁻ | | 100 | 2 | |

* Strong oxidizing agents should be removed before addition of the colour reagent.

Table 7 Some Flame atomic absorption spectrometric methods (C₂H₂/air flame) (continuous nebulization)

| Sample | separation method | Sample solution | Detection limit ng.g ⁻¹ | Remarks | Ref. |
|---|---------------------------|-----------------------|---------------------------------------|---|-------|
| Waters | Solvent extraction | DIPK-xylene | | | 37 |
| Nat. waters | Ion exchange | 6 M HCl. | 1 | | 25 |
| Al, Fe, Ni | Extraction | MIBK | 100 | Higher conc. of Sn, Bi, Cd, Pb, Zn interference | 2 |
| Phosphates | Sorption | aqueous | 12 ng | | 42 |
| Borates, Al ₂ O ₃ | | | | | |
| Manganese nodules | Ion exchange | 6 M HCl | | | 24 |
| Cement | Extraction | MIBK | 100 | Effect of 63 ions investigated | 36 |
| Blood | Extraction | MIBK | | | 2 |
| Serum | Precip. of proteins | aqueous | | | 42 |
| Liver | - | HNO ₃ /HCl | 400 | | 43 |
| Blood | Extraction | MIBK | 80 | | 45 |
| Salts of: Al, Mn, Na, K, Ca, Sr, Ba | Coprecipitation, Sorption | HNO ₃ | 30 | 50 µl injection | 18,26 |
| Minerals, Coal | Sorption | HNO ₃ | 10 | Pt-loop 10 µl | 46 |

Table 8 Some Tl determinations using GF-AAS.

| Sample | Separation | Injected Solution | Detection Limit (ng.g ⁻¹ or ng.mL ⁻¹) | Remarks | References |
|-----------------|------------|---|---|--|------------|
| Acid solutions | - | HNO ₃ , HClO ₄ , H ₂ SO ₄ , HCl | - | | 47 |
| Waters | Extraction | DIPK/xylene | 5 | Cu interferes | 37 |
| Urine | Extraction | MIBK | 1.5 | none detected | 48 |
| Blood | - | Haemolysate + La ³⁺ | 100 | | 49 |
| Cement | Extraction | MIBK/HNO ₃ /EtOH | 5 | | 36 |
| Rocks | Extraction | 5 % ascorbic acid | 0.05 ng | no investigation of interferences | |
| Rocks | Extraction | MIBK | 40 | | 36 |
| Marine sediment | Extraction | toluene/H ₂ SO ₄ | 10 | interferences from Fe, Mo, Re, W, Au, Sb, Ta | 2 |
| Co, Ni | | H ₂ SO ₄ /HF/H ₂ O ₂ | 200 | | 52 |
| Steel | | HNO ₃ | | | 53 |
| Ni-alloys | | HNO ₃ /HF | | | 54 |

Table 9 Some emission spectrometric determinations using spark or arc excitation

| Matrix | Sample pretreatment | Electrodes | Excitation mode | wavelength (nm) | Comments | Detection limit (ng.g ⁻¹) | Ref. |
|------------------------|--|------------|-----------------|-----------------|-----------------|---------------------------------------|------|
| Se | Digestion: sulphate residue | Graphite | Arc 8 A d-c | 276.8 | | 4 | 2 |
| | Digestion: chloride residue | " | Arc 13 A d-c | | | 5 | 55 |
| Pb, Bi | Fusion with PbCl ₂ | " | Arc 15 A d-c | 276.8 | Pd int.stand. | 20 | 2 |
| TiO ₂ | Fusion with AgCl ₂ | " | Arc 10 A d-c | | | 100 | 2 |
| Sn | Fusion with SnCl ₂ | " | Arc 11 A d-c | 276.8 | | 600. | 2 |
| Ga, GaAs | Electrolytic separation | " | Arc 8 A d-c | 276.8 | | | 2 |
| Dust | Low temperature ashing | " | Arc 4 A a-c | 351.9 | Bi, Sr, interf. | | 2 |
| Ash of plants | Mixed with Al ₂ O ₃ /CaCO ₃ /K ₂ CO ₃ | " | Arc 13 A a-c | 276.8 | int.stand. | 1000 | 2 |
| Minerals | Fusion with NaCl | " | Arc 20 A a-c | 291.8 and 323.0 | | | 2 |
| Urine | Residue mixed with CuO/LiF | " | Arc 4.5 d-c | | | 10 | 56 |
| (Fe(OH) ₃) | Coprecipitation with Fe(OH) ₃ | " | Arc 0.5A a-c | 276.8 | | | 2 |
| NaCl | | Al | Spark, 12kV | 276.8 | | 5 | 9 |

Table 10 Some Tl-determinations with emission spectrometry with plasma excitation

| Matrix | Excitation | Power (kW) | Gases | Wavelength (nm) | Detection limit ($\mu\text{g}\cdot\text{mL}^{-1}$) | References |
|--|------------|------------|-------------------|----------------------------|--|------------|
| Aq. solution | ICP | 1.1 | Ar/Ar | choice of line | | 33 |
| Aq. solution | ICP | 1.2 | | depending on interferences | | 35 |
| Aq. solution | ICP | 5 | Ar/N ₂ | 190.8 | | 2 |
| Aq. solution | ICP | 0.7 | Ar | | 0.2 | 57 |
| Glass | ICP | 1.5 | Ar/Ar | 351.9 | 0.007 | 58 |
| Cement, iron ores | ICP | 4.5 | Ar/N ₂ | 276.8 | 2 | 46 |
| Zn | ICP | 1 | | 535.1 | 0.2 - 2 | 2 |
| Steel | ICP | 4 | Ar/N ₂ | 276.8 | | 59 |
| Aq. solution | MIP | 0.025 | HCl/Ar | 276.8 | 0.1 ng | 60 |
| HNO ₃ | MIP | 0.020 | Ar | 377.6 | 0.015 | 61 |
| Cs- and Cd-sulphates, NH ₄ -phosphate | CMP | 0.200 | Ar/N ₂ | 377.6 | 0.4 | 62 |
| Cs ₂ SO ₄ | CMP | | N ₂ | 535.1 | 0.05 | 63 |

With excitation techniques such as ICP, CMP or MIP, the detection limits are similar. Moreover calibration is simpler (e.g. standard additions) and the methods are more reliable. A detection limit of 15 ng.mL⁻¹ Tl has been achieved with MIP excitation (61). Table 9 and 10 present a surveys of techniques with classical excitation, and plasma excitation, respectively.

The practical lower limits of detection in simultaneous multi-element determinations of Tl by ES depends considerably on the type of sample, the characteristics of the instruments and the excitation mode. In multi-element determinations, the lower limits of detection are always higher than when a single element determination is carried out after an appropriate separation. After a separation, cross interferences by other elements in the excitation step or spectral interferences (e.g. at the 276.8 nm wavelength by e or at 377.6 nm by V and even by Ca, Ni and Ti) are circumvented.

4.5. Voltammetric techniques

For Tl most authors apply inverse voltammetric techniques (64, 65), which are summarized in Table 11. Those techniques involve the best combination of sensitivity and selectivity of all methods discussed. The lower limit of detection of Tl is about 0.1 ng.mL⁻¹. Higher concentration salts (marine water) do not interfere. The major requirement of voltammetric techniques, namely that all organic matter should be digested completely, must be emphasized here, as well as in all other applications of the techniques. The extensive expertise, time and labour requirements of voltammetric techniques, is also encountered with Tl determination.

5. CONCLUSIONS

The determination of Tl from most matrices at the $\mu\text{g}\cdot\text{mL}^{-1}$ level is nowadays a relatively simple task, for which FAAS is the method to be recommended.

A universal analytical procedure for the determination of Tl at the ng.g⁻¹ level does not yet exist, although this level is common in most matrices of environmental importance. Some recommendations can be made, however. These concern favourable combinations of methods suited for certain types of matrices. Table 12 presents a summary of such recommendations.

Table 11 Some inverse voltammetric Tl-determinations

| Sample | Digestion | Electrolyte | Electrode | Electrolysis parameters | No interference from | Detection Limit (ng.mL ⁻¹) | Ref. |
|------------------|-------------------------------------|--------------------------|-------------------------------|-------------------------|------------------------------------|--|------|
| Aq. solution | | pH 4.8; EDTA detergent | Hg drop | -0.9 V vs SCE | Bi, Cu, Sb | | 66 |
| Natural waters | | pH 4.5; EDTA acetate | Hg drop | -0.8 V vs Ag/AgCl | Cd, Pb | 0.5 | 67 |
| Natural waters | | pH 4.5; EDTA acetate | Hg film | -0.8 V vs Ag/AgCl | (Cu interferes) | 0.011 | 67 |
| Sea water | | EDTA | Hg film | -1.1 V | Cd, Pb | 40 | 68 |
| Sea water | | pH 3.5; KNO ₃ | Hg film | -0.9 V vs SCE | Pb, Cu | 0.6 | 69 |
| Sea water | | KNO ₃ /DCTA | Hg film | -1.2 V vs Ag/AgCl | Cu, Pb, Cd, Zn, Bi, Co, Ni, Sn, Fe | | |
| Urine | H ₂ SO ₄ | pH 4.5; acetate/EDTA | Hg drop | -1.0 V vs SCE | | 500 | 2 |
| Serum | HNO ₃ /HClO ₄ | pH 6.4; acetate/EDTA | Hg drop | -1.25 V (15 min) | (Cu, Cd, Pb, determined also) | 10 | 2 |
| Biotic materials | LTA | EDTA | Pt Amalgamate | -1.1 V | (separation necessary) | 1 | 2 |
| Biotic materials | LTA | EDTA | Cu Amalgamate Disc (2000 rpm) | -0.85 vs SCE (10 min) | (Pb, Cd, determined also) | 0.09 | 71 |
| Rock | evaporation | pH 7-8; EDTA citrate | Hg drop | -0.75 vs SCE | (separation necessary) | | 10 |
| Rock | HF/HClO ₄ | pH 4.6; EDTA acetate | Hg drop | -0.75 vs SCE | | | 72 |
| Dust, Rain | | pH 4.5; EDTA tartrate | Hg drop | -0.8 V vs SCE | | | 73 |
| Cd-salts | | EDTA/PEG | Hg drop | -0.74 V vs SCE | | 200 | 74 |
| Salts | | pH 4.5; EDTA | Hg drop | -0.6 V vs CSE | Pb, Cd, Sn, Cu, Sb, Bi | | 75 |

Table 12 Recommended combinations of techniques

| Matrix | Digestion | Separation | Determination | Possibility to determine more Elements | Detection Limit (ng.g ⁻¹ or ng.mL ⁻¹) | Ref. |
|-----------------------|--|------------------------|-------------------|--|--|----------|
| Water | | Ion exchange | ES | yes | | 76 |
| Sea water | | Ion exchange | DPASV | some | | 77 |
| | | - | Spectrophotometry | no | 1 | 23 |
| Acids | | Sorption | ES | yes | | 46 |
| Metals | | Sorption | DPASV | | | 10,78 |
| Salts | | Extraction | Spectrophotometry | some | 2 | 73,75,31 |
| Minerals; Rocks; Ores | Pressurized, with HNO ₃ /HF | Sorption or Extraction | ICP-ES | yes | 2000 | 46 |
| | Pressurized with HNO ₃ /HF | Extraction | Spectrophotometry | no | 100 | 31 |
| | Gas (combustion) | Extraction | Spectrophotometry | no | 50 | 31 |
| | Gas (combustion) | Extraction | AAS | no | 2 | 5 |
| | Gas (combustion) | - | DPASV | some | 1 | 10 |
| | Combustion "Trace-O-Mat" | Extraction | Spectrophotometry | no | 50 | 31 |
| | Combustion "Trace-O-Mat" | - | DPASV | some | 1 | 10 |
| | Pressurized with HNO ₃ /HF | Extraction | AAS | no | 5 | 36,50,79 |
| Biotic materials | Pressurised with HNO ₃ or HNO ₃ /HClO ₄ | - | DPASV | some | 10 | 10,66 |
| | Gas (combustion) | - | DPASV | some | 1 | 10 |
| | Combustion "Trace-O-Mat" | - | DPASV | some | 4 | 10 |

Before applying such an optimal combination of digestion, separation, concentration and final measurement at the lower ng.g⁻¹ level, one should carefully check the accuracy and general performance with the particular kind of matrix. This is best done by participation in inter-comparisons, controls with different methods, use of (certified) reference materials, etc. (70).

For the determination of other elements together with TL using the same procedure, the lower limits of detection are increased and the reliability of the results may be decreased. Here, as in many other cases, a separation step prior to the final measurement gives the most accurate and precise results. A measurement with a multi-element technique (e.g. XRF, ICP-ES, ICP-MS, DPASV, etc;) can be recommended after a preconcentration step in which a group separation is involved. Optimal detection power and reliable results can be best achieved by ICP-MS.

Direct determination of the solid sample in atomic spectrometry (e.g. solid sample ICP-ES, ET-AAS, etc;) could be tried for TL as for other elements only if reference materials of a very similar matrix are available. Such certified reference materials are so far, not available in ng.g⁻¹ levels.

Good results are mainly dependent on the critical attitude, the experience and ability of the analytical chemist.

ABBREVIATIONS

| | | | |
|-------|---|----------|---|
| AA | Pentanol-2 (Isoamyl alcohol) | FAAS | Flame AAS |
| AAC | Isoamyl acetate | GF-AAS | Graphite furnace AAS |
| AAS | Atomic absorption spectrometry | ICP | Inductively coupled plasma |
| APDC | NH ₄ -pyrrolidinedithiocarbamate | KTPB | Potassium tetrphenylborate |
| CMP | Capacitively coupled microwave plasma | HMA-HMDC | Hexamethylene ammonium hexamethylenedithiocarbamate |
| DCTA | Dicyclohexyltetraacetate | LTA | Low temperature ashing |
| DDTC | Diethyldithiocarbamate | MIBK | Methylisobutylketone |
| DE | Ethoxy-ethane (diethyl ether) | MIP | Microwave induced plasma |
| DIPK | Diisopropylketone | PAN | 1-(2-pyridylazo)-2-naphthol |
| DPASV | Differential pulse anodic stripping voltammetry | PEG | Polyethyleneglycole |
| DPE | Diisopropylketone | THF | Tetrahydrofurane |
| EDTA | Ethylenediaminetetraacetate | TBM | Thiodibenzoylmethane |
| EtOH | Ethanol | TOA | Tri-n-octylamine |
| ES | Emission spectrometry | TOPO | Tri-n-octylphosphine oxide |
| | | TTA | Thenoyltrifluoroacetone |
| | | SCE | Saturated calomel electrode |

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