

INTERNATIONAL UNION OF PURE
AND APPLIED CHEMISTRY

ANALYTICAL CHEMISTRY DIVISION

COMMISSION ON MICROCHEMICAL TECHNIQUES
AND TRACE ANALYSIS*

**Investigation of Methods and Sources of Error in
TRACE ELEMENT ANALYSIS
IN SURFACE WATERS**

**Using the Determination of Chromium and Mercury
as Examples**

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INVESTIGATION OF METHODS AND SOURCES OF ERROR IN TRACE ELEMENT ANALYSIS IN SURFACE WATERS USING THE DETERMINATION OF CHROMIUM AND MERCURY AS EXAMPLES

Abstract - A survey is given of methods for the determination of chromium and mercury in various water types, mainly published in the period '75-'80.

Mercury was chosen because in this period intensive research of its determination has already been done over a rather long period. In the case of chromium, analytical research was relatively young. Accordingly there was found to be some agreement on the method to be selected for the determination of mercury. Improvements here were already more detailed. Some attention was given to sample treatment and sampling. There is a severe risk that automation of the end-determination indirectly causes errors.

There is a need in the fields of pollution and environmental analysis for analytical methods e.g. the determination of several metals dissolved in all kinds of water. The field is in full development, which means that the number of papers is very large and that there has not yet crystallised a clear cut opinion on methods and techniques. Something has been done to obtain a better overview of the field; many interlaboratory analysis rounds have been organized regionally or even on an international scale. The result of this effort is not always encouraging as the organisers often cannot predict the stability and homogeneity of their samples. On the other hand, the discrepancy usually is large, even if the same technique of end-determination is applied. More rigid instructions have to be given and a quality control system has to be set up to obtain good agreement finally (see e.g. ref. 93).

The element traces are present in different types of surface water as different species, ranging from purely ionic forms to covalent bound metals. In addition, the elements occur as dissolved or as adsorbed (to floating particles) species. When the particles are very small, they will be sedimented only very slowly. Sometimes, therefore, the adsorbed elements will be regarded as being dissolved.

The total amount is the sum of all the species. However, these species may have a different toxicity and, therefore, knowledge of speciation is desirable.

Most of the time it is not possible to make a good speciation. The methods are still in development and there is often no general agreement on the meaning of the results. So for this contribution we focussed on total determination methods.

One should define first of all the aim of the analysis (water as a biotope, water for drinking water supplies...) before starting any determination. Water analysis with a high degree of accuracy is required for the development of models predicting the fate of pollutants in a certain environmental compartment.

A complicating factor in the evaluation of the water quality is the fact that there is a change of methods and a general improvement. The consequence is that results of a few years ago can no longer be compared with more recent results. As the development of methods proceeds and as the average laboratory quality improved, the only way to re-evaluate data from the past would be the banking of a whole set of water samples and a reassessment of methods and results with banked samples at regular intervals, (see e.g. ref. 94, 95).

In the development or introduction of new methods and techniques, the old question should be considered very thoroughly: do I really measure the compound, which I think I measure? ("Messe ich was ich zu messen glaube?").

Although one is never completely sure, frequent calibrations and intercomparisons are necessary. Reference materials might replace a part of the intercomparison work.

1. Sampling and sample conservation

The sampling is the first of a whole chain of actions building the entire analysis. Thus the sampling procedure must be given at least the same attention as given to the final measurement. The sampling procedure should be developed in close co-operation with the client, with the analyst and the statistician. Many analyses are carried out already before the final tailor-made sampling procedure is established. As soon as a sample is separated from its matrix, its own life literally starts. Biological processes proceed, precipitations occur or precipitates are dissolved due to pH-changes and the formation of complexing agents, new chemical equilibria resulting from the change of redox potential occur and so on. In other words: after a short time the sample no longer resembles the matrix from which it was separated. This problem is usually recognised. Often reagents are added immediately after sampling. These reagents should stop biological activity or dissolve all precipitates, etc.. The difficulty is that addition of these reagents (e.g. chloroform, sulphuric acid) changes the sample just as well. For example, after sulphuric acid addition, one can no longer distinguish between ionic Cd, adsorbed Cd and complex-bound Cd.

Sometimes this is not important (e.g. for the amount of heavy metals shipped by the Rhine from one country to another), but in other cases (e.g. toxicity tests) the way of binding is crucial (e.g. dimethyl-mercury or HgS). The best way so far to avoid this problem is in situ analysis of the sample, which might mean working on board ship. The chance of measurable changes in the sample is low if the analysis starts immediately after the sampling.

Here again, one must say that a tailor-made sample conservation is necessary.

2. Sample (pre)treatment

Many methods exist for the clean-up and the pre-concentration of aqueous samples. These methods range from destruction to all kinds of extraction, ion exchange and the like. A recent IUPAC report (1) deals extensively with concentration methods. Terms and definitions of this report will be used here.

The destruction of aqueous samples is difficult due to the large dilution of the reagents involved. This dilution causes a loss of efficiency. Therefore, destructions are not so frequently used. On the other hand, most of the frequently applied routine methods demand an efficient matrix removal. The solution is found in the development of extractions, ion exchange methods, co-precipitation methods and the like.

3. Summarisation of frequently used methods for Cr and Hg

Table 1 and 2 summarize methods published in the period 1975-1980. The indications are (limits of detection, concentration factors etc.) taken as they were presented by the authors of the publications. It is often unclear from the papers how authors arrive at their figures.

Mercury could be regarded as a "pars pro toto" for a group of heavy metals, known to be toxic and monitored already for years. This group may include Pb, Cd, Cu and Zn as well. Not only the toxicity caused a common interest in these metals. They are determined as well because their determination is relatively easy and their chemical behaviour is well known. Chromium is selected in this first investigation because of its toxic nature (4, 10) which is less generally understood and because of the difficulty of the determination. The Cr-content of rivers is less than 50 ng/g; in not heavily polluted seawater this content is about 0.05 ng/g.

Table 1 presents a summary of recently developed methods. Not all possible methods are included. The intention is to obtain some idea of frequently used methods. Table 2 summarises Hg-determinations.

A short general discussion of certain methods for Cr should be given first.

The diphenylcarbazide method is still in frequent use. The interferences of Cu, V and Fe can be circumvented. Cu and V react with the analytical reagent; after 40 min. and 20 min., respectively, their contribution (negative resp. positive blank) is sufficiently decreased. The interference by Cu often is overcome by standard addition techniques (38). Depending on the Fe-concentration the metal is complexed (Fluoride) or removed by extraction of the Fe-cupferron-complex into CHCl_3 .

MIBK is a frequently used extraction solvent. Due to its relatively large solubility in water, the extraction procedure is troublesome. An attractive alternative is 3-heptanone, although the efficiency in nebulization (AAS) is less (36). The extractability of Cr (III) with MIBK is poor. Therefore, a previous oxydation or an extraction procedure at high temperatures is necessary (37). All the extraction procedures may suffer from low recoveries if used in waters containing a high content of natural complexing agents. Chromium usually complexes and decomplexes slowly, causing these low recoveries even if the particular complex constants suggest no interference. The extractability of Cr(VI) with APDC, -DDTC or MIBK varies from 50-100%(70).

As in other cases, chemiluminescence is sensitive to interferences (4). The wide variability in the water matrix thus demands frequent and careful checks of matrix influences.

Inter-element effects and the oxidation state of the chromium preclude the direct determination with AAS in an air-acetylene flame (6). Flameless AAS techniques suffer from matrix influences, e.g. Na_2HPO_4 and Na_2SO_4 interfere at levels of 5 g/l and 40 g/l, whereas Fe (III) and Co (II) should not be present at 100-1000 times the Cr-amount (11).

The reduction waves of Cu interfere in the DPP-determination of Cr with ammonium acetate as a supporting electrolyte. Ethylene diamine shifts the Cu-waves due to the formation of complexes (19). Another way of overcoming interferences is the application of ASDPP (20).

In general, many methods are applied for the determination of Cr. In introducing a new method for Cr one should consider whether the Cr is hexavalent or trivalent, whether the possible extraction gives a satisfactory recovery for all Cr-species in the amount of time described and so on.

List of abbreviations used in tables 1 and 2

| | |
|-------------|---|
| AAS | : Atomic Absorption Spectrometry |
| AG1-X4 | : Strong base Ion exchanger (Bio-Rad) |
| Aliquat 336 | : Mixture of methyl tri-alkylammonium chlorides (alkyl groups: mainly C_8 mean mol.weight: 475; manuf.: General Mills, Mankakee, Ill.USA). |
| APDC | : Ammonium pyrrolidine dithiocarbamate |
| ASDPP | : Anodic Stripping, Differential Pulse Polarography |
| DDTC | : Diethyl dithiocarbamate |
| DPC | : Diphenyl carbazide |
| DPP | : Differential Pulse Polarography |
| EDTA | : Ethylene Diamine Tetraacetic Acid |
| GLC | : Gas liquid Chromatography |
| 8-HQ | : 8-hydroxy quinoline |

$$K_C : K = \frac{(Q_T/Q_M)}{(Q_T^0/Q_M^0)}, \text{ when } Q_M^0 \text{ and } Q_M \text{ are the quantities of the matrix}$$

before and after preconcentration respectively and Q_T^0 and Q_T are the quantities of the microcomponent before and after preconcentration.

| | |
|------|-------------------------------|
| MIBK | : Methyl isobutyl ketone |
| MS | : Mass spectrometry |
| NAA | : Neutron Activation Analysis |

- R : Recovery: the yield of a preconcentration step expressed as quantities of the microcomponent of the concentrated microcomponent $R = \frac{Q_T}{Q_T}$
- Usually recovery is given as: %
- S/N : Signal to noise ratio
- TFA : 1,1,1-trifluoro-2,4-pentanedione(tri fluoracetyl acetone)

The similarity between the mercury determinations is larger. As the environmental toxicity of mercury has already been understood for a longer time, more methods are developed and a glimpse of consensus arises.

The basic idea of most of the routinely used methods now is:

- i) : digestion of organic material when necessary;
- ii) : reduction of Hg(II) mostly by Sn(II);
- iii) : collection of Hg, e.g. on Au or Ag, and
- iv) : measurement by AAS, often as a "cold vapour".

The differentiation comes up if one likes to distinguish between various Hg-containing species, e.g. methylmercury compounds (HgMe) and HgCl₂.

4. REMARKS

In practical situations the selection of a method of analysis for a certain element depends on the availability of instrumentation and trained staff. Although it is recognised that electrochemistry provides the best means to determine speciation and total contents in water (e.g. As, Cd, Ni, Cu ...), atomic absorption spectrometry is by far more popular because of its ease in use and broad range of elements covered.

Automation of the end-method and the processing of the results is widespread. The risk is that the sample (pre)treatment is neglected. Often it is too easily assumed that the instruments work well. In the sample (pre)treatment one must frequently assess whether the applied chemical reactions still proceed at the same rate and with the same efficiency (preferably 100%) and whether there are differences in changing from one type of water to another or from one concentration range to another.

Another interesting feature is the often dualistic way of automation. As AAS is very popular, it is worthwhile and interesting for designers and customers to automate the whole measurement, including the calculations. The sample treatment, however, is often carried out completely in a normal way, because every sample and every element to be determined needs its own sample treatment procedure. This situation still causes errors due to human errors and increases contamination risks. It should therefore be tried to automate the sample (pre)treatment at least in such a way that less human attention is necessary and that the whole procedure can take place in a closed system. (97,98)

The time has come to pay more attention to the chemistry preceding a final measurement; research concerning the efficiency and reliability of chemical reactions at low concentration levels, the automation of the whole (pre)treatment and the development of better systems (immobilized reagents in columns?) should be supported. (96)

TABLE 1 : Determination of Cr

| (1) Matrix | (2) Sample Treatment | (3) Preconcentration |
|-----------------|--|---|
| seawater | Oxidation of Cr(III) to Cr(VI) with KMnO_4 | Extraction with ADPC in MIBK |
| water | heating for 300 s on steambath | Cr(III): extraction with 8-HQ in MIBK Cr(VI): extraction with NaDDTC in MIBK |
| water | | Cr(VI): sorption on AG1-X4 ion exchanger, elution after reduction |
| natural water | | Extraction with Na-DDTC in MIBK |
| natural water | Reduction of Cr(VI) with H_2O_2 ; NH_4ClO_4 added to obtain a uniform matrix | Evaporation of water |
| water/sea-water | | coprecipitation with $\text{Al}(\text{OH})_3$; flotation with Na oleate and N_2 |
| seawater | | coprecipitation with $\text{Fe}(\text{OH})_3$ (ref 23) followed by extraction into MIBK as acetylacetone complex |
| seawater | | extraction with DDTC in MIBK (sample vol: 1000ml MIBK vol: 30 ml) |
| seawater | | Cr(III): extraction (pH6-8) from 1M SCN with Aliquat 336 in toluene Cr(VI): extraction (pH2) with Aliquat 336 in toluene |
| seawater | formation of Cr(III)-EDTA complex for reprod. thermal decomposition | |
| water | | |
| natural water | | Cr(III): coprecipitation with $\text{Fe}(\text{OH})_3$ Cr(VI): reduction with $\text{Fe}(\text{OH})_2$ and coprecip. with $\text{Fe}(\text{OH})_3$ |
| mineral water | | coprecipitation with $\text{Fe}(\text{OH})_3$ |
| seawater | | coprecipitation with $\text{Zr}(\text{OH})_4$ from NH_3 soln |
| seawater | reaction of Cr(VI) with DPC | exchange on Dowex 50W-X ⁴ cation exchanger |

| (4) Recovery(R) Conc. Coeff. (K_c) | (5) Final Determination | (6) Limit of detection ^x (ng.g^{-1}) | (7) Nr. of ref. |
|--|---|--|--------------------|
| $K_c = 40$ | AAS in flame | 0.05 | 2 |
| $K_c = 30$ | AAS in flame | ng.g^{-1} level | 3 |
| R = 90% $K_c = 100$ | AAS in flame | 0.1 (coeff.of var. 20%) | 4 |
| $K_c = 6.5$ | AAS in flame | 2 | 5 |
| $K_c = 5$ | AAS in flame ($\text{C}_2\text{H}_2/\text{air}$) | 4.3 | 6 |
| R = 98% $K_c = 100$ resp. $K_c = 50$ | AAS in flame | ng.g^{-1} level | 7 |
| $K_c = 500$ | AAS in flame | 3 (coef.of var. 5%) | 8 |
| | AAS in flame or flameless AAS | 0.4 (flame) 0.02 (carbon furnace) | 9 |
| R = 100% $K_c = 33$ | flameless AAS of extract | 0.03 | 10 |
| R = 100% $K_c = 100$ | flameless AAS of extract | 0.01 | |
| | carbon rod AAS(1 μl sample at 3000°C) | 0.005 (S/N=2) | 11 |
| | flameless AAS with Ta-filament (2400°C) 0.5 μl sample | 0.05 ml sample | 12 |
| R = 90% $K_c = 140$ | flameless AAS carbon furnace | 0.001 (S/N=2) | 13 |
| $K_c = 20$ | flameless AAS | 0.08 (coeff.of var.15%) | 14 |
| | flameless AAS | ng.g^{-1} level | 15 |
| | spectrophotometer | 0.1 (S/N=2) | 16 |

Table 1 contd.

| (1) Matrix | (2) Sample Treatment | (3) Preconcentration |
|---------------|---|--|
| water | for total Cr: oxidation of Cr(III) with KMnO_4 for Cr(VI) only: precipitation of $\text{Cr}(\text{OH})_3$ | |
| natural water | masking of Cr(III) with salicylic acid | coprecipitation with BaSO_4 |
| seawater | total Cr: reduction of Cr(VI) with SO_2 | Cr(III): coprecipitation with $\text{Fe}(\text{OH})_3$, separation of Cr from Fe by anion exchange, oxidation of Cr(III) |
| seawater | | Cr(III): coprecipitation with $\text{Al}(\text{OH})_3$ Cr(VI) in filtrate after coprecip.: red. with NH_2OH |
| water | addition of ethylenediamine to mask Cu | |
| water | | |
| water | masking of interfering metals with EDTA | |
| water | reduction of Cr(VI) | |
| tapwater | | coprecipitation with PbSO_4 |
| natural water | reduction of Cr(VI) with Na_2SO_3 | complexation with TFA; extraction into benzene |
| seawater | | freeze drying |
| water | oxidation of Cr(III) to Cr(VI) | ion exchange |
| seawater | reduction of Cr(VI) with Na_2SO_3 | adsorption on active charcoal |
| water | complexation with 1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octanedione | |
| seawater | oxidation of Cr(III) with Ce(IV) | extraction with APDC into CHCl_3 |
| water | evaporation of H_2O ; drying of residue; mixing with NaCl and C | |
| water | | electrodeposition (const. current) upon pyrolytic graphite electrode |

| (4) Recovery(R) Conc. Coeff. (K_c) | (5) Final Determination | (6) Limit of detection ^x ($ng.g^{-1}$) | (7) Nr. of ref. |
|--|---|---|--------------------|
| | spectrophotometer with DPC | 5 | 17 |
| $K_c = 125$ | spectrophotometer with DPC | 0.02 (S/N=2) | 18 |
| R = 99% $K_c = 80$ | spectrophotometer with DPC | 0.5 | 23 |
| R = 97% $K_c = 120$ | spectrophotometer with DPC | 0.3 0.5 | 24 |
| | DPP | 10 | 19 |
| | DPP ASDPP | 2.5 1.5 | 20 |
| | chemiluminescence | 0.03(S/N=2) | 21 |
| | chemiluminescence | 60 (1-2% coeff. of var.) | 22 |
| | solid state reflec- tance of precipitate | 3 | 25 |
| R = 95% $K_c = 1$ | GLC | 0.1 | 26,27 |
| | NAA | 0.5(coeff.of var.8%) | 28 |
| | NAA | 1.8(coeff.of var.10%) | 29 |
| sample vol. 300 ml charcoal:20mg | NAA | 0.05(coeff.of var. 20%) | 31 |
| | MS | sub pg-level | 30 |
| | MS | 0.001 | 32 |
| | Arc emission | 30(coeff.of var.14%) | 33 |
| | | 2000 | 34 |

TABLE 2 : Methods for the determination of mercury

| (1) Matrix | (2) Sample Treatment | (3) Preconcentration |
|--|---|---|
| Riverwater | Sample acidif.(HCl) Inorg.Hg: red. Sn(II)/H ₂ SO ₄ Total Hg: destr.(15min) ² at 30°C with HClO ₄ /H ₂ O ₂ , subs. red. Sn(II) | |
| Water | Sn(II)-reduction | Sorption on Ag-wool subs. heating in Ar 650/700 ml/min |
| Water | Sn(II)-reduction | |
| Synth.seawater Springwater | sample adjusted pH 6.5-7.5 (spring) or pH 9 (seawater) | extraction of MeHg with benzene, with alamine 336-S (aminemixture) separation with g.c. |
| Org. Hg in natural waters | 50 ml sample, acidif. (HCl) destr. of org. Hg with BrO ₃ /Br (1 min) | |
| Surface, spring groundwater | | electrolytical (8-10hrs) separation from sample (1 l) on gold electrode. heating of gold.Gasflow 600 ml/min |
| Seawater, lake- water, synth. sample | interlab. study (17 labs) sample acidif. (pH 0.5, H ₂ SO ₄) Sn(II)-red. (10%) | 1) Ag or Au wool 2) KMnO ₄ sol. 3) none |
| Natural water synth. soln | Polyolefin sample bottles (50 ml) cleaned with CHCl ₃ followed by HCl/HNO ₃ -vapours digestion HNO ₃ /K ₂ Cr ₂ O ₇ subs. K ₂ S ₂ O ₈ Sn(II)-red. vapourization in air stream | |
| Water | 4 l sample. Sn(II)/HCl-red.; aeration 5h, 0.6 l/min) (or:1.5 l/min;80°C for ½ hr) | absorption in 20ml KMnO ₄ / aeration (2l/min) H ₂ SO ₄ ; Sn(II)-red. |
| Glacial ice | Acidified (HNO ₃) sample irradiated Ascorbic acid (5min) Sn(II)-red. | Hg diss. in HNO ₃ ; precip. as Hg S ²⁺ |
| Seawater | 450ml sample, acidif.(HNO ₃) Sn(II)-red.; Ar-aeration (140ml/min during 40 min) | sorption on Au, subs heating (300°C), Ar-flow(180ml/min) |
| Seawater | inorg.Hg:coprecip.with CdS from acid. soln (HCl) subs. flotation Add. of surfactant(octadecyl- trimethyl ammoniumchloride in ethanol) org.Hg: digestion (24 h) with KMnO ₄ /H ₂ SO ₄ | the froth is dissolved in HNO ₃ /HCl. Sn(II)-red. |

| (4) Final Determination | (5) Recovery (R) Conc.Coeff.(K _c) limit of detection | (6) Reference |
|-----------------------------------|---|------------------|
| AAS | Range: 1-15 ppt Stand.dev. 1ppt (at 15 ppt-level) | 87 |
| microwave induced Ar-plasma | 3.10 ⁻¹⁷ range: 10 ⁻¹⁴ -10 ⁻⁷ g or pg/l-level R = 100% | 88 |
| AFS | 5 ppt or 5 pg rel.precis: 5% above 50 ppt range: 1-100 ppt | 89 |
| microwave induced plasma (em.) | 4-10.10 ⁻¹² g MeHg 1-2.5 ng/l coeff. of var. 10-15% (at 10 ng/l-level) K _c = 10-200 | 90 |
| AAS | R=95-102% | 91 |
| AAS | 1.5 ng/l | 39 |
| AAS | results for synthetic samples are better | 92 |
| NAA | Values higher than AAS-values | |
| AAS | Loss in 15 days:10% | 81 |
| AAS | 2ng/l (4 l sample K _c = 200 R _c = 100% | 82 |
| NAA | 0.3ng(2xstand.dev.) instrum. back ground | 83 |
| AAS | limit of detn.:0.47ng typ.value in sea- water:12.9ng/l (stand.dev. 0.60 ng/l) | 84 |
| flameless AAS | 0.02µg/l R=80-90% coeff. of var.:14% (at 0.01 µg/l) | 85 |

Table 2 contd.

| (1) Matrix | (2) Sample Treatment | (3) Preconcentration |
|-----------------------------------|---|---|
| several environ- mental waters | ads. on charcoal; Sn(II)-red. | |
| Fresh, saline waters | UV-photo oxidation | red. |
| Fresh water | Digest.: $\text{HNO}_3/\text{H}_2\text{O}_2$ | Anion exchange column |
| Fresh water | | solubilized (Cu(II) dithi- zionate containing triton X-100 at pH=1 |
| Seawater | sample (50ml) is degassed (30min) electrolysis at -0.5V for 60 min. | electrodep. (1h) at -0.5V |
| Seawater | digestion: $\text{HNO}_3/\text{K}_2\text{Cr}_2\text{O}_7$ or $\text{HNO}_3/\text{H}_2\text{SO}_4$ | preconc. with Pb-diethyldithio carbamate in CHCl_3 (pH 2-3) |
| Fresh saline waters | UV-digestion in presence of H_2SO_4 | Sn(II)-red. |
| Natural waters | stream of air or inert gas through sample | Trapping in KI_3 -soln; reduct. by alkaline ascorbic acid soln. |
| Surface water | digest.: $\text{K}_2\text{Cr}_2\text{O}_7/\text{H}_2\text{SO}_4$ (UV-light) | extr. into benzene |
| Water | | trapping of HgMe and Hg(II) on polyurethane foam carrying dithizone; elution with acet. |
| Water | complexation with pyrrolidine carbodithionate extraction with propylene carbonate. Reduction by SnCl_2 and sweep with N_2 | aeration |
| Water | Oxid. with H_2SO_4 , KMnO_4 $\text{K}_2\text{S}_2\text{O}_8$ at 105°C . | red.; aeration |
| River/lake water | digest.: KMnO_4 , H_2SO_4 and $\text{K}_2\text{S}_2\text{O}_8$ | Sn(II)/ H_2SO_4 -red. |
| Water | Inorg. Hg: Sn(II)/ H_2SO_4 -red. Org. Hg: removal of inorg. Hg by red. and aeration; subs red. with Sn(II)/NaOH (12M) | aeration, gas transport to cell |
| Drinking water | destr. with Br_2 ; red. of excess with NH_2OH | Sn(II)-red.; aeration |
| Seawater | | trapping on macroreticular chelating resin contg. episulfide groups. Elution 4M HCl of HgMe; extr. with glutathione/benzene |

| (4) Final Determination | (5) Recovery (R) Conc. Coeff. (K_c) limit detection | (6) Reference |
|--|--|------------------|
| NAA | 1 ng/l R=98-100% | 86 |
| AAS (cold vapour) | 0.02 $\mu\text{g/l}$ (water) R 90-110% (stand. addition) | 40 |
| NAA | 7×10^{-3} $\mu\text{g/l}$ R = 80% coeff. of var.: 10% | 41 |
| dual wavelength spectro- photometry (507 & 493nm) | 0.05-0.25 μg (5 ppt) | 42 |
| ASDPP | $K_c=1$ 5 $\mu\text{g/l}$ S.d 10% | 43 |
| NAA | R = 98% $K_c=50$ | 44 |
| AAS (cold vapour) | 0.02 $\mu\text{g/l}$ prec.: 0.07 $\mu\text{g/l}$ 6% about 0.55 $\mu\text{g/l}$ 1% about R = 90% | 45 |
| AAS | limit of detn.: 6.10^{-4} μg (3 ml sample) | 46 |
| AAS or GC/MS | | 47 |
| | Hg-conc. 10ppm | 48 |
| AAS | range: 5-500 ng/l | 49 |
| AAS | 0.2 $\mu\text{g/l}$ stand. dev. 0.04 $\mu\text{g/l}$ (at 0.5 $\mu\text{g/l}$) 0.84 $\mu\text{g/l}$ (at 20 $\mu\text{g/l}$) R=92-125% (depending on kind of water) | 50 |

Table 2 contd.

| (1) Matrix | (2) Sample Treatment | (3) Preconcentration |
|----------------------|--|---|
| Natural waters | digest: 1 l sample with $\text{KMnO}_4/\text{H}_2\text{SO}_4$; red. of Hg(II) | aeration Hg trapped on Au; subs heating |
| Natural sea-water | | hydrophobic gel (in CHCl_3 swollen polystyrene beads) containing dithizone traps Hg(II) (pH 1) Elution with 8M HCl |
| Water | | column (containing 0.25-0.30 g trioctylamine) chromatography (80-100ml/l) drying eluate on a polyethylene pad Irradiation before extraction (lubricating base oil). After irradiation add. of 1mg Hg (carrier) and 15 ml conc. HClO_4 ; org. material digest.: $\text{K}_2\text{Cr}_2\text{O}_7$ |
| Surface and seawater | 2500 ml sample 1) 500 ml det. of suspend. matter and total Hg filtration through charcoal 2) 2000 ml - flow through centriugation a) 1000 ml inorg. Hg, red., volatilization, adsorption on charcoal b) 1000 ml act. charcoal total Hg | |
| Water | digest.: KMnO_4 (room temp.) $\text{K}_2\text{S}_2\text{O}_8$ (95 °C) | red. |
| Wastewater | | coprecip. wit protein by lignin derivates (pH 4); filtration |
| Water | | Sn(II)-red.; trapping of Hg on Ag-wool in a quartz tube; heating of amalgam (400 °C) |
| Water | extraction; chromatography | |
| Water | | preconc. on emission spectroscopic carbon powder as pyrrolidinedithiocarbamate complex at pH 6-8 and 50°C, filtration and drying |
| Seawater | | preconc. on 3 cm PbS column at pH 1 ($\text{HNO}_3/\text{H}_2\text{SO}_4$) |
| Natural waters | Sn(II)-red. during 3weeks | Hg-vapours collected on porous Ag subs. heating to 500 °C in N_2 -stream |
| Lakewater | | Sn(II)-red. (1l); aeration 1.5 l/min (30min) Hg trapped in $\text{KMnO}_4/\text{H}_2\text{SO}_4$ sol |
| Water | | precip. as protein/tannic acid compl. (pH 5) ovalbumine |

| (4) Final Determination | (5) Recovery (R) Conc.Coeff.(K _c limit detection | (6) Reference |
|--|--|------------------|
| flameless AAS | 0.005-0.05 g/l HgMe | 54 |
| AAS | R=95% at 0.01 ppt lev. (MeHg lower) | 55 |
| NAA | conc. reported to be successful at ppm and ppb levels | 56 |
| NAA | limit of detn.: 6.2×10^{-9} g/l coeff. of var.: 10-12% | 57 |
| NAA | limit of detn.: 0.25×10^{-8} g/ml | 58 |
| NAA (volatilization) and adsorption on a fresh C-bed | 1 ng/l | 59 |
| coldvapour flameless AAS | 0.06 ppm (in 100 mg sample) coeff.of var.: 4% | 60 |
| AAS | | 61 |
| AAS | 0.25 ng/l; coeff.of var.: 6.8% (at 14 ng/l) | 62 |
| NAA | limit of detn.: 1.5×10^{-9} g/ml (extr.) 1.1×10^{-11} (chrom) | 63 |
| NAA | 0.01 ppt Hg | 64 |
| NAA | R=98% | 65 |
| AAS | coeff.of variation 10% for 5 ng Hg | 66 |
| flameless AAS | range: 0.5-2.4 μ g/l K _c =200 | 67 |
| AAS | | 68 |

Table 2 contd.

| (1) Matrix | (2) Sample Treatment | (3) Preconcentration |
|--|---|---|
| Water | digest.: HNO_3 , HCl , H_2O_2 ; pH 4.5 (NH_3) | extr. with thiotheonyl- trifluoro acetone (TTA) in benzene. Excess TTA removed with $\text{H}_3\text{BO}_3/\text{NaOH}$ (pH 11) |
| Water | | conc. on anionic exchange paper |
| Natural waters | flowthrough UV-digestor | |
| Natural/waste water | digestion: $\text{KMnO}_4/\text{K}_2\text{S}_2\text{O}_8$ | reduction |
| Rainwater lakewater | | Hg(I)-extraction with dithizone; back-extr. with HCl 1:1 |
| Drinking water | | red. with NaBH_4 |
| Not specified | | electrodep. on pyrol. graphite electr. (90 min) |
| Seawater (zooplankton) marine sedim. | 100 ml sample acidif. (HNO_3) digest.: UV-photo-oxidation | Sn(II)-red.; aeration with N_2 (7min; 0.5 l/min) cold trap (liq. N_2). Finally heating |
| Natural water | digest.: 5ml sample in sealed ampoule $\text{K}_2\text{S}_2\text{O}_8/\text{H}_3\text{PO}_4$ at 120 °C | Sn(II) red. |
| Seawater | (comparison of pyrex and po- lyethylene containers) Digest: $\text{HNO}_3/\text{KMnO}_4$, $\text{K}_2\text{S}_2\text{O}_8$ at 80°C (2h) | Sn(II)/ H_2SO_4 -red. |
| | study of storage conditions | |
| Natural water | photodigestion of acidif. samples | aeration |

| (4) | (5) | (6) |
|---------------------|---|-----------|
| Final Determination | Recovery (R) Conc.Coeff.(K _c limit detection | Reference |
| AAS | range: 0.01-2ppm error: 5% | 69 |
| XRF | 20 µg/l | 70 |
| AAS (cold vapour) | 0.02 µg/l prec.6% at 0.07 µg/l | 71 |
| AAS | | 72 |
| AAS | | 73 |
| flameless AAS | 0.004 ppm | 74 |
| XRF | range: 1-5 µg/l 20% (1 µg) coeff.of var. 2%(5µg) | 75 |
| flameless AAS | 2 ng/l | 76 |
| AAS | range:1-100 ppt or 5-500 ng coeff.of var.:4-2% R=95-100% | 78 |
| AAS | range:0.009-0.13 µg/l coeff.ofvar.:14%-1.5% (pyrex and acidif sample best results) (pH=1.5) | 78 |
| radiotracers | best cond. K ₂ Cr ₂ O ₇ /HNO ₃ (pH 0.5) Au(III)/HNO ₃ (pH 0.5) | 79 |
| AAS (cold vapour) | 0.03 µg/l R = 100% | 80 |

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