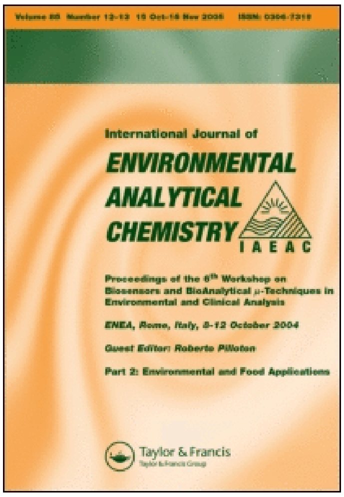

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# The Determination of Arsenic in Soil and Sediment Digests by Graphite Furnace Atomic Absorption Spectrometry

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# The Determination of Arsenic in Soil and Sediment Digests by Graphite Furnace Atomic Absorption Spectrometry

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A method for the determination of As in siliceous materials from a fluoboric acid matrix by GFAAS is described. The basic analytical procedure also permits the measurement of major, minor and other trace elements by flame or graphite furnace AAS as appropriate. For As analysis, the incorporation of matrix modification with Ni and of corrective measures to overcome interference by Al, Na and Si are discussed. The validity of the method is demonstrated by the accurate analysis of four international standard reference materials and agreement with instrumental neutron activation analysis results for As in environmental samples. One application to the study of As geochemistry in lacustrine sediments is presented.

KEY WORDS: Arsenic, soil, sediment, graphite furnace atomic absorption spectrometry.

## INTRODUCTION

In recent years there has been great interest in developing satisfactory procedures for the determination of As in siliceous materials such as soils and sediments. Most methods, with the notable exception of the relatively costly non-destructive instrumental neutron activation analysis,[1–5] entail initial sample digestion and subsequent conversion of dissolved As to a chemical form suitable for measurement. Reduction to $AsH_3$ by either $KI/SnCl_2/Zn$ or $NaBH_4$ is commonly employed. The liberated gas may then be collected or complexed for Gutzeit analysis[6] or colorimetry (via complexing with molybdenum blue[7–8] or silver diethyldithiocarbamate[9–11]), introduced to an $Ar/H_2$ flame,[12–13] quartz tube,[9,14–22] or graphite furnace[23] for atomic absorption spectrometry, to an inductively coupled plasma[24-25] or DC plasma arc[26] for emission spectrometry[27] or to an $Ar/H_2$ flame for atomic fluorescence spectrometry.[28] As in other fields of As analysis, the most commonly used technique is atomic absorption spectrometry. There has been a great diversity of methods for initial sample digestion although most involve attack by single mineral acids[15,21,23,24] or a combination of acids e.g.

$HNO_3/H_2SO_4$,[19] $HNO_3/HClO_4$,[15,16,28] $HCl/HNO_3$,[13,20]

$HNO_3/HClO_4/HF$,[27,30] $HNO_3/HClO_4/HF/KMnO_4$,[12,22]

$H_2SO_4/K_2S_2O_8$,[17]

or an initial fusion e.g. by

$KHSO_4$,[6,9] NaOH,[25] KOH/MgO.[18]

The occurrence of many associated problems with respect to efficiency of dissolution procedures, potential loss of As, the influence of valence state on $AsH_3$ generation and interferences in the atomic absorption measurement step itself have been reviewed by Agemian and Bedek.[22]

With the apparent preference for hydride generation and quartz-cell AAS, graphite furnace atomic absorption spectrometry (GFAAS) has not been employed to any great extent in the determination of As in soil or sediment digests. Despite the use of Ni compounds in matrix modification steps,[31] many workers[32-34] still consider the GFAAS determination of As in environmental samples, even in relatively uncomplicated matrices such as water, to be extremely difficult and often unreliable because of severe interferences in the atomization step. In our laboratory, we have recently modified and developed an analytical method which permits the determination of major and minor elements in siliceous materials from a fluoboric acid matrix by flame ($N_2O/C_2H_2$) AAS[35-42] to enable the direct determination of several trace elements (e.g. Cd, Cr, Cu, Pb) in the same solution by GFAAS.[43] Similar success, notably for Cd in silicates,[44] has been reported by other workers.[45-46] This paper describes the application of this method to As analysis by GFAAS, the identification and resolution of several severe interference problems, the subsequent verification of the modified procedure by the accurate measurement of As in four international standard reference materials of soil, sediment and atmospheric particulate matter and one application in the field of environmental geochemistry to the determination of As in a freshwater sediment core.

## EXPERIMENTAL

### Dissolution procedure

For 0.1 g samples, the procedure consists of (a) the decomposition of moistened sample using 1 ml aqua regia and 7 ml HF in a capped 125-ml polypropylene container at 90°C on a water bath and (b) the addition of 50 ml of a filtered, saturated solution of $H_3BO_3$ and further heating at 90–100°C. Minimum heating times of 1 hr for both (a) and (b) are required for 0.1 g samples. After complete dissolution, 5 ml of 2% KCl is added as an ionization buffer for major element determination in the $N_2O/C_2H_2$ flame and the final volume is adjusted to 100 ml with $H_2O$ via monitoring of solution weight (102 g).

For samples greater than 0.1 g, quantities of acids and lengths of heating times should be increased as found necessary to achieve complete dissolution.

Aristar grade (B.D.H.) $HNO_3$, HCl and HF, Analar $H_3BO_3$ and KCl, and deionised, distilled water were used throughout.

### Standard solutions

A range of As working standard solutions of up to 0.8 mg/l were prepared in a reagent matrix of $HCl/HNO_3/HF/H_3BO_3/KCl$, identical to that of the samples, from successive dilutions of a stock 1000 mg/l As ($AsCl_3$) AA spectroscopy standard (B.D.H.). In routine operation, these solutions are also made 0.2% in Ni via the addition of $Ni(NO_3)_2$ solution as discussed below under matrix modification. Composite multi-element standards of major and minor elements were also prepared in the reagent matrix up to concentrations of 100 mg/l Al, 30 mg/l Ca, 100 mg/l Fe, 30 mg/l Mg, 5 mg/l Mn, 10 mg/l Na, 300 mg/l Si and 2 mg/l Zn.

### Instrumentation

A Perkin–Elmer HGA-74 graphite furnace, attached to a Perkin–Elmer Model 306 atomic absorption spectrophotometer equipped with a $D_2$ arc background corrector, was employed for the determination of As at the 193.7 nm resonance line emitted by a Perkin–Elmer As electrodeless discharge lamp at a power setting of 8W. Slit setting was 0.7 nm. Sample volumes of 20 μl were injected into the furnace by an AS-1 autosampler. Ordinary graphite tubes, sheathed with Ar, were used and absorbances were recorded as peak heights on a Kipp and Zonen BD8 chart recorder.

## Operating conditions and matrix modification

Ashing/atomization curves were constructed for As under a variety of solution conditions. An increase in ashing temperature from 300°C to 1000°C was enabled by the addition of Ni (0.2%) to 1% $HNO_3$ solutions of As, a matrix modification procedure now commonly employed in the determination of volatile elements like As and Se.[29,31,47–48] For the fluoboric acid reagent matrix, similarly adjusted to 0.2% Ni, identical settings to those derived for 0.2% Ni/1% $HNO_3$ were obtained for the ashing (1000°C) and atomization (2500°C) temperatures. The complete temperature programme employed, using the gas-stop facility during atomization for As concentrations up to 0.4 mg/l, was:— dry—105°C (30s); ash—1000°C (30s); atomization—2500°C (12s); burn-out—2700°C (6s).

Increases in sensitivity of 100% and 30% were obtained for 0.2% Ni/1% $HNO_3$ As standard solutions over 0.005% Ni/1% $HNO_3$ and 0.1% Ni/1% $HNO_3$ respectively. The fluoboric acid reagent matrix, without Ni, caused a 50% reduction in As sensitivity relative to 0.2% Ni/1% $HNO_3$ but modification to 0.2% Ni reduced this deficit to 25%. In the case of this latter solution, the calibration curve of absorbance and As concentration was linear to 0.4 mg/l for 20 μl injections. For prepared sample solutions, Ni can be added either to the total sample, during or after sample volume adjustment to 100 ml, or to a separate aliquot.

In this work, major elements, e.g. Al, were determined in a $N_2O/C_2H_2$ flame using the flame conditions and instrumental settings recommended by the manufacturer,[49] employing burner rotation where necessary to reduce sensitivity.

## Standard reference materials

In the development of this analytical method, four standard reference materials were analysed:— NBS SRM 1645 River Sediment, NBS SRM 1648 Urban Particulate Matter, IAEA Soil-5 and IAEA SL-1 Lake Sediment. Several aliquots in the range 0.05–1 g were dissolved.

## RESULTS AND DISCUSSION

In the initial stages of this analytical study, direct As analysis of solutions of varying weights of the three standard reference materials SRM 1645, Soil-5 and SL-1 yielded very unreliable data, a mixture of low, accurate and elevated values. It was observed, however, that substantial improvements were achieved on successive dilutions of the more concentrated sample solutions with reagent blank. This suggested the existence of significant interferences perhaps associated with the major ion composition of the solutions, a phenomenon not observed in our GFAAS studies on other trace elements (Cd, Cu, Cr, Pb) in fluoboric acid digests.[43]

Interference effects of several major ions on As absorption have been reported by several workers.[32-34] For example, Chakraborti *et al.*[33] found a large depression of the As signal when Na or K and $SO_4^{2-}$ were present together in solution at concentration levels exceeding a few mg/l while Al apparently enhanced the signal at concentrations >4 mg/l. On the basis of these reports and of our own empirical observations of a possible relationship between the extent of interference affecting As and the concentration of Al (and not simply of *total* solids) in sample solutions, we conducted an experiment on the influence of Al on apparent As absorbance under reagent matrix conditions. Figure 1 illustrates the enhancing effect of Al on absorbance at the 193.7 nm line, leading to the elevated apparent As concentrations. The effect appears to be As-

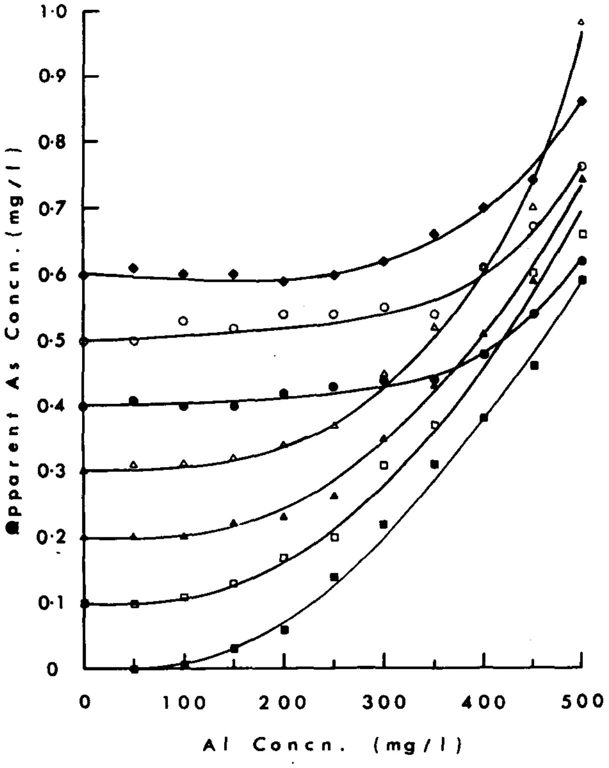

FIGURE 1 The effect of increasing Al concentration (0–500 mg/l) on the apparent As concentration in a 0.2% Ni/fluoboric acid reagent matrix for As standard solutions of concentration (mg/l) 0(■), 0.1(□), 0.2(▲), 0.3(△), 0.4(●), 0.5(○) and 0.6(◆).

concentration dependent. The spiking with Al of those standard reference material sample solutions which had yielded correct As results produced similar enhancements. Exhaustive investigation of sample solutions of SRM 1645, Soil-5 and SL-1 showed that accurate As values were invariably obtained when the Al concentration was ≦60 mg/l and, on occasion, in the range 60–100 mg/l (e.g. SL-1) (N.B. solution As concentrations <0.4 mg/l) provided that the Si concentration was <300 mg/l, a finding of particular significance for SRM 1645 with its much higher Si/Al ratio. Irrespective of the initial weight of sample dissolved, appropriate dilution with Ni-modified reagent blank to Al concentrations ≦60 mg/l, with Si correspondingly <300 mg/l, following Al and Si determination in the $N_2O/C_2H_2$ flame, yielded As data in agreement with certificated values for the reference materials.

While, as fully discussed below, the incorporation of the above dilution step to overcome Al interference produced an acceptable and widely applicable analytical method for As in siliceous materials, it failed to explain apparent *reductions* in As concentration in more concentrated sample solutions for *some* standard reference materials where Al concentrations were much greater than 60 mg/l (Table I). For reasons similar to those in the case of Al we investigated the effect of Si and Na on apparent As concentration over a range of As standard solutions both with and without the addition of Al. It was found that Si, both on its own and in the presence of 60 mg/l Al, could be tolerated at levels of 300 mg/l, suppressive effects on the As signal being limited to <10%, but that an unacceptable reduction in As signal of 35% occurred at 1000 mg/l Si. For Na, our results demonstrated a suppression effect the extent of which was dependent on both As and Al concentration (Figure 2) explaining, at least qualitatively in conjunction with Si data, decreases in As values for SRM

TABLE I

Examples of the effects of sample solution dilution on apparent arsenic concentrations of some standard reference materials

| | | Direct analysis | | Dilution | | |
|---|---|---|---|---|---|---|
| Material | Wt. (g) | Al (mg/l) | As (mg/kg) | Factor | Al (mg/l) | As (mg/kg) |
| N.B.S. | 0.1 | 24 | 67 | — | 24 | 67 |
| SRM-1645 | 0.3 | 73 | 49 | 2 | 37 | 66 |
| (66 mg/kg) | 0.5 | 121 | 46 | 3 | 40 | 61 |
| I.A.E.A. | 0.1 | 100 | 30 | 2 | 50 | 30 |
| SL-1 | 0.3 | 300 | 62 | 4 | 75 | 27 |
| (27.5 mg/kg) | 0.5 | 500 | 73 | 6 | 83 | 29 |

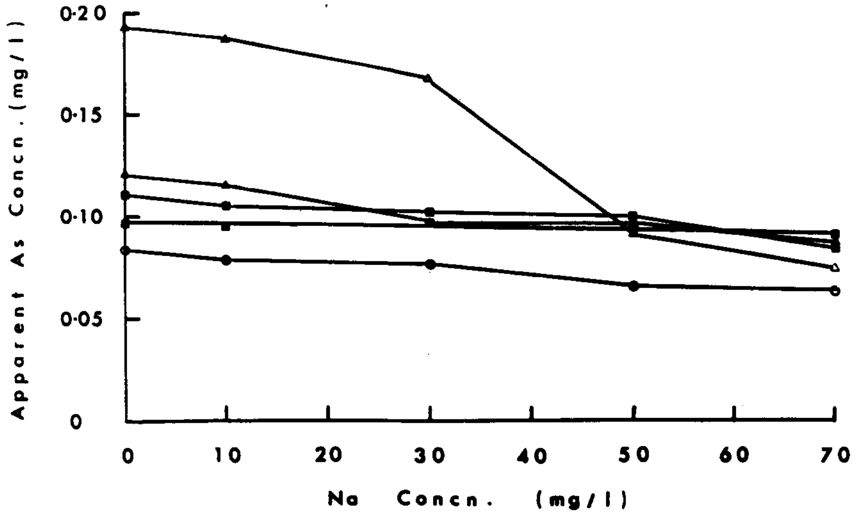

FIGURE 2 The effect of Na (0–70 mg/l), in the presence of Al, on apparent As concentration for 0.1 mg/l. As standard solutions in a 0.2% Ni/fluoboric acid reagent matrix of Al concentration (mg/l) 50(■), 100(□), 150(▲), 200(△) and for a 0.05 mg/l As solution 200 mg/l (○) in Al.

1645 and Soil-5 but increases for SL-1 at Al concentrations substantially in excess of 60 mg/l. In part, these phenomena reflect sample Na/Al concentration ratios of 0.23, 0.23 and 0.017 and corresponding As/Al ratios of $2.73 \times 10^{-3}$, $1.15 \times 10^{-3}$ and $2.75 \times 10^{-4}$ for SRM 1645, Soil-5 and SL-1 respectively. As accurate As values were obtained for SRM 1645 and Soil-5 at Al concentrations <60 mg/l, it would appear that Na concentrations up to at least 14 mg/l are tolerated in this Al concentration range, certainly for As concentrations up to 0.07 mg/l (Table II).

It is equally difficult to resolve the nature of these typical interferences in As analysis, usually described as "non-specific absorption", and to explain the success of this method for the determination of As and other trace elements in siliceous materials by GFAAS. In contrast, the proven applicability of the method to the measurement of major and minor elements by flame AAS has been attributed to the reduction of potential interferences through use of the 3000°C $N_2O/C_2H_2$ flame and the predominance of the fluoborate anion.[35–42] It is quite possible that other species, in addition to Al and Na, may also interfere at the 193.7 nm As line in the graphite furnace. Furthermore, non-specific absorption interferences may also be complemented by sample matrix effects on the rate of release of As at the atomization temperature, although the addition of Ni to sample solutions, effective in stabilisation of As at the ashing

TABLE II

Major and minor element concentrations (mg/l) in solutions of standard reference materials normalized to aluminium concentrations of 60 mg/l

| | N.B.S. SRM 1645 | N.B.S. SRM 1648 | I.A.E.A. Soil-5 | I.A.E.A. SL-1 |
|---|---|---|---|---|
| Al | 60 | 60 | 60 | 60 |
| Ca[a] | 72 | 112 | 17 | 1.8 |
| Fe | 280 | 71 | 33 | 40 |
| K | (30) | (18) | 14 | (9) |
| Mg[a] | 19 | 14 | 9.4 | 4.0 |
| Mn | 1.9 | 1.5[a] | 0.6 | 2.1 |
| Na | (14) | (7.3) | 14 | 1.0 |
| Si[a] | 759 | 295 | 260 | 184 |
| Ti | | (7.3) | (3.4) | 3.1 |
| Sample wt. (g) | 0.25 | 0.18 | 0.073 | 0.06 |
| As | 0.16 | 0.21 | 0.069 | 0.017 |

N.B.

1. ( )—non-certificated values.
2. [a]—values based on Farmer and Gibson data (Table III)[43].
3. 500 mg/l should be added to each K concentration because of addition of 5 ml 2% KCl to each solution.
4. Other notable cations include 73 mg/l Cr and 4.3 mg/l Zn in SRM 1645, 12 mg/l Pb and 8.7 mg/l Zn in SRM 1648.

stage, may counteract both effects.[34] We plan to investigate the nature of interferences on As still further using more sophisticated furnace technology in the shape of the HGA-400 and the stabilized temperature platform furnace.[50–51] However, it is our experience, with the HGA-74, that our analytical procedure, with Al $\leq$ 60 mg/l, is successful for the typical range of major ion concentrations encountered although we would normally advise a further 2-fold dilution (i.e. Al $\leq$ 30 mg/l) as an additional check provided sufficient As is present in the sample solution. Table II lists the major ion concentrations for each standard reference material solution normalized to Al = 60 mg/l. It should be noted that no problems were experienced with NBS SRM 1648 Urban Particulate Matter (Na/Al = 0.12, As/Al = $3.48 \times 10^{-3}$), accurate As results always being obtained within the weight range 0.05–0.18 g.

Fundamental requirements for the successful determination of As in the $HCl/HNO_3/HF/H_3BO_3$ digests of siliceous materials thus include matrix modification with Ni, adequate background correction to help counter non-specific absorption—the $D_2$ arc matching the signal from the As electrodeless discharge lamp operating at a maximum power setting of 8W—and dilution of Al to $\leq$ 60 mg/l. The mean As data from ten separate analyses of the four standard reference materials, performed under optimum analytical conditions, are compared with certificate values in Table III. Although the As level for NBS SRM 1645 has not been officially certified by NBS, values of 66 mg/kg,[22] 66.4 mg/kg[25] and 69 mg/kg[4] have also been reported by independent investigators. Greenberg[52] found 117 ± 5 mg/kg for NBS SRM 1648 while 95.1 mg/kg and 100 mg/kg were obtained for Soil-5 by Goulden *et al.*[25] and Agemian and Bedek[22] respectively.

TABLE III

Determination of arsenic (mg/kg) in NBS and IAEA standard reference materials by GFAAS

| | Measured | Certificated |
|---|---|---|
| NBS SRM 1645 | | |
| River sediment | 66.6 ± 4.3 | (66) |
| NBS SRM 1648 | | |
| Urban particulate matter | 113 ± 12 | 115 ± 10 |
| IAEA Soil-5 | | |
| Soil | 102 ± 6 | 93.9 ± 7.5 |
| IAEA SL-1 | | |
| Lake sediment | 29.9 ± 2.7 | 27.5 ± 2.9 |

N.B.
Measured values represent the mean (± 1$\sigma$) of 10 analyses.

Under optimum conditions the detection limit for As is 0.002 mg/l for a 20 $\mu$l injection with reagent blanks generally $\leqq$ 0.002 mg/l (N.B. high initial blanks of 0.05–0.1 mg/l were associated with the use of *Analar* HF). Precision (R.S.D.) on multiple injections of 0.1 mg/l samples and standards by the AS-1 autosampler was typically better than ± 2% (± 1$\sigma$). In view of the As detection limit of 0.002 mg/l and the additional constraint of Al $\leqq$ 60 mg/l in the analyte solution, an expression for the detection limit for As in siliceous samples can be derived—0.33$x$ mg/kg where $x$ is the Al concentration of the sample in per cent. Thus, for a typical Al concentration of 8% the As detection limit would be 2.7 mg/kg.

The method is appropriate for geochemical and environmental studies on soil, sediment, street dirt, atmospheric particulates, etc. One application in our laboratory has been the investigation of As geochemistry in the sediment column of freshwater Loch Lomond following the discovery of unusually elevated As concentrations in surface sediment by Farmer and Cross[3] using an instrumental neutron activation analysis technique. A typical profile is displayed in Figure 3, the vertical structure being attributable to post-depositional diagenetic effects rather than to any

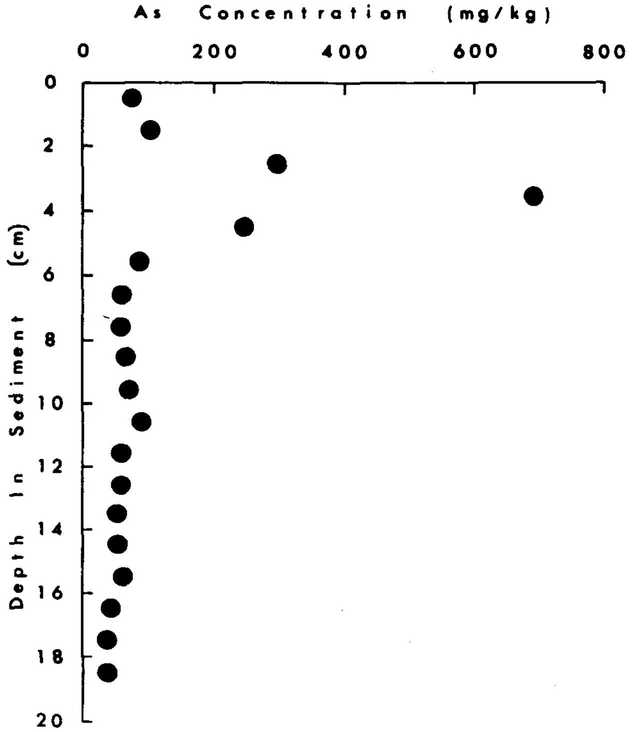

FIGURE 3 Concentration of As (mg/kg) in sediment core LL-5 (collected 15 Dec. 1981, water depth 19 m) from the southern basin of Loch Lomond.

major input via environmental pollution sources.[3,53–54] In addition to values for *total* As in siliceous materials, the method may also be useful in investigations of As speciation and partitioning among various chemical and mineralogical phases based on sequential chemical leaching techniques.[21,55–56] Measurement of As in intermediate residues can yield, by difference, the levels previously removed, possibly into solution matrices unsuitable for direct As estimation. The results of such a study will be included in a comprehensive discussion of As geochemistry in Loch Lomond sediment currently in preparation.[54]

Several of the sectional As values for the Loch Lomond sediment core (Figure 3) were checked by neutron activation analysis, the excellent agreement (Table IV) providing additional confirmatory evidence that the analytical procedure described by Farmer and Gibson[43] for the direct determination of trace elements by GFAAS and major elements by flame AAS in the same fluoboric acid solution is also suitable, in modified form, for measurement of As by GFAAS.

TABLE IV

Comparison of arsenic determinations in sediment sections from a Loch Lomond Core (LL-5) by GFAAS and INAA

| Depth in sediment (cm) | As concentration (mg/kg) GFAAS | INAA |
|---|---|---|
| 3–4 | 690±20 | 700±20 |
| 10–11 | 89±6 | 92±4 |
| 18–19 | 37±2 | 34±6 |

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