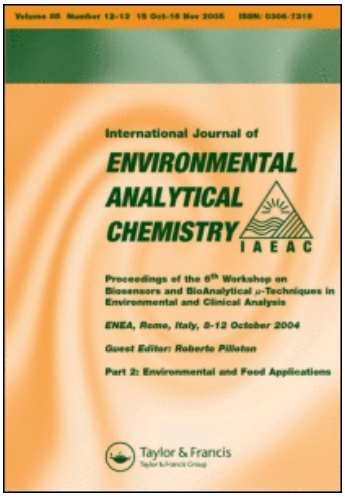

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Atom Reservoir Atomic Absorption. Application to Marine Environmental Samples†‡

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KEY WORDS: flameless atomic absorption, sea water, biological tissues, sediments, trace metals.

The application of flameless atom reservoir atomic absorption spectrophotometry to the analysis of trace metals in marine water, sediment and biota, and air particulate samples is discussed. Methods are described for the analysis of a range of metals including Cu, Fe, Co, Ni, Cd, Ag, Zn, and Pb in these samples. Recent developments of atomizer design, primarily the static method of analysis and the grooved graphite tube are utilized, significantly improving the sensitivities attainable and the speed of analysis.

INTRODUCTION

The application of flameless atomization to atomic absorption and atomic fluorescence spectrophotometry has considerably improved the absolute sensitivities attainable by either of these two related techniques. For most elements, the sensitivities are improved by two to three orders of magnitude, compared to conventional flame atomization.

The development of flameless atom reservoirs which has taken place over a number of years has been adequately reviewed.[1] Despite the long

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history of development the introduction of the technique to applications in the analysis of environmental samples has taken place only recently, concurrent with the development of commercially available atomizers.[2-5]

The flameless atomization technique is uniquely suited to many analyses of environmental samples because of its extremely high sensitivity and very small sample requirements. Thus, many analyses for trace elements which, with other determination techniques, require extensive preconcentration from large samples can be carried out efficiently with very small samples and little chemical workup. The sensitivity afforded by the flameless atomic spectroscopic techniques is for most elements comparable and for many elements better than that attainable with neutron activation, a technique which is instrumentally considerably more complex and beyond the range of possibility for the average laboratory.

Despite the extremely high promise of flameless atomization several disadvantages are also apparent. With the currently available instrumentation the speed of analysis and the precision of the flameless techniques is not as good as that obtained with the flame atomizer; analysis of the very refactory elements is not yet possible; interference effects are significantly different from those in the flame (also between different flameless atomizer designs) and not yet well documented; and the small sample required for analysis is often not representative unless great care is taken.

Flameless atomic spectroscopy has been applied to the analysis of fresh waters,[6-8] saline waters,[9-12] biological tissues,[11,13-16] sedimentary material,[17] geological materials,[8,18-20] oils,[21-24] air particulates,[15,25-26] beer,[15] brain tissue, blood and serum,[8,27-34] urine,[28,35] fingernails,[36] synthetic fibres,[36,37] plastics and paper,[36] and milk.[4]

This paper is concerned with the application of flameless atom reservoir techniques to marine environmental samples: saline water, sediments, biological tissues, and air particulates.

SALINE WATERS

The sensitivities attainable with flameless atomic absorption spectrophotometry are such that direct analysis of natural water samples utilizing volumes of less than 100 mcl is possible.[6,7,10] The analysis is subject to a number of interferences related to the matrix composition. In samples with low total dissolved salt concentrations the non-specific background absorption due to molecular absorption or scattering of light may be compensated by use of a deuterium arc background corrector. However, standard addition measurements show that in natural low salt content samples the matrix reduces the response for a given addition of many metals when compared to

aqueous standards.[6] It is postulated that this effect might be due to changes in the rate of volatilization of the analysis element which may lead to a broader but lower output peak.[38] Thus, it would appear to be inherently more satisfactory to measure the peak area of the output signal and not, as is conventional, the peak height. An alternative or, perhaps, additional matrix effect may exist. As the density of matrix atoms in the atom cloud increases, the chances of recombination of the analysis element with atoms of other elements increase, thus lowering the peak equilibrium atom population and consequently the output signal.

Because of these matrix problems it is necessary to utilize the standard additions technique even with low salt content natural waters. The matrix effects that are observed with low salt content waters are compounded when marine or other saline waters are investigated. The quantity of total salts in the matrix is such that upon atomization the molecular and scattering absorption is sufficient to totally (or almost totally) attenuate the light-beam. Under these conditions even the use of the deuterium arc background corrector cannot compensate for the interference.[10] Accordingly, it was found necessary to employ a selective volatilization technique to determine trace metals in saline water samples.[9,10] This technique involves the removal of the major salt bulk at temperatures below that required to volatilize the analysis element with subsequent atomization of this element at high temperature. This technique works well for the more refractory elements, e.g., Fe, V and also for some of the moderately refractory elements, e.g., Co, Ni, Cu, and Mn. However, for this latter group of elements there is a significant but reproducible amount of co-volatilization of the analysis element with the salt matrix and thus the sensitivity is reduced.[10] It has proven impossible to determine the less volatile elements by selective volatilization, since, although they are atomized from simple aqueous solutions at temperatures below that required to volatilize the major matrix elements, the matrix prevents their atomization until the temperature is sufficient to atomize the major matrix elements themselves.

Some recent advances in the technique of flameless atomic absorption spectrophotometry, notably better hollow cathode lamps and the 'static' method of analysis,[39] have led to some significant improvements in the analytical sensitivities for most elements. The static analysis method alone has improved detection limits for various elements by between 1.5 times and about 5 times. This improvement is achieved simply by stopping the gas flow in the heated graphite atomizer tube at the instant atomization of the analysis element and restoring the flow only after the output peak has been passed. Thus, the atoms are swept out of the light-beam more slowly; the gas temperature within the atomizer is probably maintained somewhat higher and the peak atom population is increased. Utilizing this technique we have been able

TABLE I

Detection limits for direct injection analysis of sea water (salinity ≃ 35°/oo)[a]

Element	Detection limit (mcg/l)
Co	10
Cu	10
Mn	3
Ni	10
Fe	1
V	30

[a] Utilizing static analysis technique.[39]

to obtain somewhat better detection limits than previously reported for the direct analysis of sea water for trace transition elements[10] (Table I). These improvements in detection limits increase the potential of the technique for use in monitoring for contamination of saline waters by Co, Cu, Mn, Ni, Cr, and V. However, for these elements the sensitivity is still too poor for oceanographic use in the open oceans. The improved detection limits for Fe are such that it is now possible to determine this element in marine coastal waters waters with a precision acceptable for many purposes. One interesting result of the use of this technique is the observation that even the 'dissolved' Fe (passes a 0.45-micron filter) is non-uniformly dispersed in sea water in such a manner that a 20-mcl sample is non-representative. Thus, the average of a series of analyses of 20 mcl of filtered unacidified sea water is the same as that of the same sample acidified. However, the scatter of analytical results is considerably greater in the unacidified sample, whereas the scatter in the acidified sample is only that normally induced by the experimental technique.[40]

Direct injection analysis of sea water for most trace elements is not possible, as the attainable sensitivities are only marginally good enough and there is a severe matrix interference problem. Thus, a preconcentration and separation of trace metals from the salt matrix appear to be necessary for most analyses. Because there are few interelemental interferences among trace transition metals in atomic absorption determinations unless the atom ratios are abnormally high, it is advantageous to utilize a separation procedure which does not discriminate strongly between transition elements but which separates these elements efficiently from the major group I and II cations and the anions. The solvent extraction of the transition metal pyrrolidine dithiocarbamates into a ketone is one such technique which has been used extensively for separation prior to flame atomic absorption

TABLE II

Analysis of sea water by ammonium pyrrolidine dithiocarbamate/ MIBK extraction and atomic absorption

Element	Seawater concentration[a] (ng/l)	Approximate detection limits (ng/l)		
		Flame[b]	Direct injection of ketone[c]	Ashing and injection of aqueous soln.[d]
Ag	100	100	0.4	0.05
Cd	50	40	0.6	0.1
Co	80	200	24	2
Cu	3000	50	14	2
Fe	3000	300	10	1
Ni	2000	400	120	10
Pb	30	400	5	1
V	1500	500	2000[e]	25
Zn	5000	50	0.2	0.05

[a] From Riley and Chester.[44]
[b] 500 ml of sea water extracted with 15 ml ketone, final volume was adjusted to 10 ml; flame aspiration.
[c] 500 ml of sea water extracted with 15 ml ketone, final volume was adjusted to 10 ml and injection of 50 mcl into heated graphite atomizer with grooved tube.
[d] 500 ml of sea water extracted with ketone. Ashing residue of ketone solution was dissolved in 5 ml of 1N HNO_3; 100 mcl injection into heated graphite atomizer with standard tube.
[e] Grooved tube cannot be used with HGA–70. Refers to 5 mcl injection in standard tube.

analysis.[41–43] The elements Ag, Co, Cd, Cu, Fe, Ni, Pb, Zn and possibly others can be quantitatively extracted from 500 ml sea water into 15 ml of methylisobutyl ketone at pH 3–4 with the addition of 4 ml of a 10% solution of ammonium pyrrolidine dithiocarbamate. Using flame atomic absorption the detection limits are such that only Zn, Cu, and Ni and in coastal waters Fe and Pb can be determined with adequate precision in this extract. Analysis of this ketone extract by flameless atomic absorption using normal atomizers offers very little advantage.[11] Because of the low surface tension of the ketone compared to water only 5 mcl of the ketone may be introduced into the heated graphite atomizer, as larger injections lead to partial loss of the sample from the ends of the tube during drying. To overcome this problem the metals may be reverted back to aqueous solution, when the detection limits become more than adequate to determine each of the listed elements in oceanic waters (Table II). This reversion to aqueous solution is tedious and may contribute significantly to the blanks. Acid back extraction is not quantitative and it is necessary to evaporate the ketone, destroy the organic matrix and dissolve the metals in nitric acid.[11, 14] Recently, a new graphite tube design has been introduced (Perkin-Elmer Part No. 040–6088) which allows the introduction of up to 50 mcl of ketone solution into the Perkin-Elmer HGA–2000 without

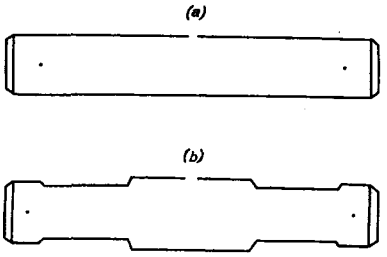

FIGURE 1 Graphite tubes: (a) normal design; (b) grooved pattern.

sample loss during evaporation. These tubes have a groove running around the center portion of the tube within which the solution is retained during evaporation (Figure 1). Thus the ketone extract may be analyzed directly by injection into the atomizer fitted with this type of tube. The detection limits obtained are not as good as those obtainable after reversion to aqueous solution, but for most of the elements considered they are adequate for precise analysis of oceanic waters (Table II). The detection limits are poorer than obtained with samples reverted to aqueous solution, because a smaller fraction of the total sample is injected into the atomizer and because the performance characteristics of the new tube are different from the original straight configuration (Table III). The maximum temperature reached with the grooved

TABLE III

Relative detection limits obtainable for standard tube and grooved tube[a]

	Approximate detection limit (picogram)	
Element	Standard tube	Grooved tube
Ag	2	4
Cd	2	3
Co	100	300
Cu	40	70
Fe	10	25
Ni	200	600
Pb	20	25
V	500	—
Zn	2	2

[a] These detection limits were not determined under optimum conditions but were calculated from peak heights for higher concentrations and average noise level and are representative of everyday working limits. They serve to compare performance with the different tubes.

tube is lower than can be obtained with standard tubes (ca. 2350°C compared to 2520°C with HGA–2000 power supply; HGA–70 gives somewhat lower temperature). Thus atomization of the less volatile elements is slower and indeed the temperature is insufficient to atomize vanadium when using the HGA–70 power supply. In addition, the volume of the atom cloud in the new tubes is somewhat increased and a larger proportion of the atoms lies outside the light-beam and thus does not contribute to the absorption signal. However, it is possible to improve the detection limits by multiple injections of ketone solution with drying between each injection. This multiple injection technique gives more reproducible results with the grooved tube than with the standard tubes, presumably because the sample is constrained in the groove during drying and thus deposited more uniformly in successive injections. Detection limits listed in Table II for direct injection of ketone may be improved by a factor of two or three by successive injections.

The analysis of the methylisobutyl ketone extracts of pyrrolidine dithiocarbamates from single samples of between 500 and 1000 ml of sea water employing direct injection of the ketone into a grooved tube with a Perkin-Elmer HGA–2000 heated graphite atomizer is now being routinely used for the analysis of Ag, Co, Cd, Cu, Ni, Zn, Pb, and Fe in coastal and oceanic sea waters. Analysis of the ketone extract must be carried out as soon as possible after the extraction and in any event within 36 hr, as the metal complexes are not indefinitely stable in ketone solution. Full details of this technique are to be published elsewhere.[45]

In addition to multi-element analysis using relatively large volumes of water as described above it is possible to carry out similar analyses using volumes of sea water of less than 50 ml to determine concentrations of Zn and Cu in ocean water, and most of the elements discussed above in polluted estuarine water. The use of such small sample volumes permits a more rapid and convenient analysis procedure and reduces the sample collection requirements.

BIOLOGICAL TISSUE

The importance of assessing the biological impact of trace metal or radionuclide pollution is such that a very large number of analyses of the tissues of marine organisms for trace elements have been carried out in the past[46] and will undoubtedly be required in the future. Ideally, analytical techniques should require only small samples, be capable of determining a number of elements in each sample, be capable of handling large numbers of samples, and require instrumentation which is inexpensive and simple enough to be used by even the smallest of laboratories. The flameless atomic absorption

technique is undoubtedly the best alternative available at this time when all of these requirements are considered together.

A number of possible procedures can be employed in the analysis of biological tissues by flameless atomic absorption, primarily the analysis of the sample after ashing, dissolution and any necessary chemical separation; the direct analysis of solid wet or dry tissue samples; or the analysis of finely dispersed solid samples. Each of these techniques may find application for some analyses of different tissue types, but it would appear that a general method for multi-element analysis of a range of different tissue types must at present involve the dissolution of the sample and a separation of the trace metals from the major salt matrix.

Ideally, analysis of biological tissues would be carried out by direct introduction of the solid sample either dried or better still wet directly into the atomizer. This technique may indeed by applicable to the analysis of certain elements in specified tissue types, but a number of problems have been encountered which dictate that considerable study of the analytical procedure will be necessary for each such application. The drawbacks include the long drying times necessary for the analysis of wet samples, and the non-uniform heating of solid samples unless they are powdered or introduced in a manner by which they are in uniform contact with the tantalum boat container. Generally the ashing of a tissue sample leaves a significant carbon residue which with the major element residue gives rise to a considerable scattering or molecular absorption signal, except when using very small samples. Attempts to utilize selective volatilization with solid tissue samples are not generally successful. The presence of appreciable amounts of refractory elements such as Ca or Si gives rise to a non-specific absorption signal even at high temperatures after an intermediate temperature selective volatilization step. In addition, the complex and variable nature of the matrix gives rise to non-reproducible amounts of co-volatilization during the intermediate temperature selective volatilization step. An additional problem with solid samples is that dilution is not possible and thus the dynamic range is limited by the maximum sample that produces an acceptable non-specific absorption signal (generally less than 2 mg) and by the smallest sample than can be accurately and easily weighed (a few tenths of a milligram).

As direct introduction of the solid tissue sample does not appear to be a generally applicable analysis procedure, it would appear that it is normally necessary to dissolve the sample. This may be achieved by a number of procedures, but the method of choice is perhaps wet ashing with concentrated nitric acid,[13,14] a procedure which although somewhat slow leads to the smallest possible blanks. Because of the extremely high sensitivity of the flameless atomic absorption technique considerable effort must be expended to maintain low blanks. The solution from the nitric acid ashing may be used

TABLE IV

Approximate detection limits for analysis of biological tissues

Element	Detection limit (ng/g dry wt.)	
	Standard tube[a]	Grooved tube[b]
Ag	0.02	0.2
Cd	0.03	0.2
Co	0.5	6.0
Cu	0.5	3.0
Fe	0.4	4.0
Mn	0.4	4.0
Ni	2.0	25.0
Pb	0.3	2.0
V	5.0	—
Zn	0.02	0.08

[a] 1 g Sample. Ashed. Extracted into ketone, reverted to 5 ml 0.1N HNO_3. Injection volume 100 mcl.
[b] 1 g Sample. Ashed. Extracted into ketone. Volume adjusted to 10 ml. Injection volume 50 mcl.

for direct injection analysis with the flameless atomizers. However, major matrix problems are encountered for the analysis of most elements and tissues, so that it may be concluded that a general analysis technique must involve the separation of the trace metals from the dissolved matrix. As for the saline water samples the extraction of the pyrrolidine dithiocarbamates of the trace metals into a ketone is an ideal technique and has been employed routinely for this purpose. The use of nitric acid wet ashing, pyrrolidine dithiocarbamate extraction, reversion to aqueous solution, and flameless atomic absorption for multi-element analysis have been discussed more fully elsewhere.[13,14] However, subsequent to this study the grooved graphite tubes mentioned above have become available and it is now possible to use the ketone extract directly for analysis using these tubes instead of reverting the metals back to aqueous solution. Analytical detection limits are somewhat poorer when using the ketone solution but are generally still adequate to determine a range of elements precisely in most biological tissues (Table IV).

SEDIMENT

Flameless atomic absorption analysis of sedimentary material containing very high silica contents would appear to be possible using the aqueous solution from a hydrofluoric acid–perchloric acid digestion directly. The

matrix resulting from this digestion is relatively simple due to the loss of silica as its volatile tetrafluoride. However, most sediments contain appreciable and variable quantities of groups I and II elements and in all but the most silicon-rich sediments the dissolved matrix is complicated and concentrated enough to constitute an analytical problem. Thus, either extraction of the trace elements or possibly standard addition techniques are normally necessary.

The analytical technique including solvent extraction of the pyrrolidine dithiocarbamate complexes as applied to biological tissues can also be applied to sedimentary material, although the dissolution step is in this instance carried out with hydrofluoric and perchloric acids. In most sediments the concentrations of the trace elements considered in this paper are high enough so that if a ketone extraction of the metals from a gram or so of the sediment after dissolution were possible, determination could be carried out by flame atomic absorption. However, the concentration of iron in sediments is usually so high that the solubility of the iron pyrrolidine dithiocarbamate complex is the factor limiting the concentration of the other elements that may be achieved. That is, in order to extract all the iron quantitatively (without which other metals are not quantitatively extracted) such a large volume of ketone must be used that the concentrations of other elements in this ketone are often too low for precise determination by flame atomic absorption. Specific chelating agents (other than ammonium pyrrolidine dithiocarbamate) which do not form complexes with iron may be used, but at present no satisfactory alternative appears to be available which will chelate with a range of transition elements with the exception of iron.

The sensitivity of the flameless atomic absorption technique is such that a

TABLE V

Approximate detection limits for analysis of sedimentary material

Element	Approximate detection limit[a]
Ag	2
Cd	2
Co	60
Cu	30
Fe	40
Ni	250
Pb	20
Zn	0.8

[a] 0.1 g Sample. Dissolved in HF/$HClO_4$. Extracted into ketone. Volume adjusted to 10 ml. Injection of 50 mcl ketone using grooved tube.

ketone extract of the pyrrolidine dithiocarbamates from as little as 0.1 g of dissolved sedimentary sample normally contains high enough concentrations for precise analysis of the most of the transition elements considered (Table V). The ketone extraction of iron pyrrolidine dithiocarbamate is quantitative from this size sample except in the most iron-rich sedimentary material. Although the iron is present in very large excess in such an extracted sample it does not appear to exert a major matrix effect under the conditions of analysis. This technique will be reported more fully elsewhere. The direct analysis of volatile elements in solid rock sample has been reported but no details were given.[8] It seems likely that such techniques may be applicable to sedimentary materials for some elements if the major matrix elements do not interfere. However, it is unlikely that such techniques will be generally applicable.

AIR PARTICULATES

Because of its high sensitivity, flameless atomic absorption analysis is uniquely suited to the analysis of metals in the particulates or aerosols of the atmosphere. The determination of lead in air particulates has been reported either by collection of the particles on a membrane filter, acid dissolution and analysis of the solution[25] or more elegantly by utilization of a graphite crucible for filtration of the air and then the introduction of this crucible directly into a graphite tube furnace.[26] Beryllium in air particulates has been determined by collection on organic membranes, destruction of the membranes with acetone in the atomizer, and ashing and analysis of the residue.[15] Recently, a number of elements have been determined in air particulates collected with a standard high-volume air sampler (Environmental Protection Agency) on fibre glass filters. The filters are treated with concentrated nitric acid, the residue is centrifuged, and analysis is carried out on the solution.[47]

Undoubtedly, the flameless atomic absorption spectrophotometric technique will find applications in the analysis of over-ocean aerosols, an area of great current interest.

CONCLUSIONS

Flameless atomic absorption spectrophotometry has already become a powerful tool for the analysis of marine environmental samples: water, biota, sediments and air particulates. However, the instrumentation is by no means optimized at present and there has been little time for develop-

ment of more exotic applications. It is certain that the extremely high sensitivities that may be obtained for some of the rarer elements which are not mentioned in this paper will be used to develop analytical techniques for these elements in the marine environment. Thus, because of the small samples required and the speed of analysis it will be possible to investigate the biogeochemical cycles of these elements in the oceans more completely than has been possible until now.

Acknowledgments

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