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SIMPLEX OPTIMIZATION OF CONDITIONS FOR THE DETERMINATION OF ARSENIC IN ENVIRONMENTAL SAMPLES BY USING ELECTROTHERMAL ATOMIC ABSORPTION SPECTROMETRY

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Summary—Simplex optimization was used to efficiently delineate the optimum experimental conditions to be used for the electrothermal atomic absorption spectrometric analysis of arsenic in a standard reference material of marine origin. Four experimental variables, were considered: ashing temperature, atomization temperature, modifier concentration, and atomization ramping time. This combination of methods and materials provides a powerful means of rapidly improving the experimental conditions used for analysis of arsenic in a wide variety of samples of environmental origin. Excellent recoveries of arsenic were obtained when using the optimum electrothermal atomic absorption spectrometry conditions to analyze standard solutions of arsenobetaine, arsenocholine and tetramethylarsonium iodide.

Electrothermal atomic absorption spectrometry (ETAAS) has been widely used for the determination of arsenic in biological, geological, marine and fresh water samples.[1–4] The United States Environmental Protection Agency recommends ETAAS methods for the determination of a number of trace elements, including arsenic. Low detection limits, good precision, simplicity in operation as well as minimum sample pretreatment are all features which have contributed to the widespread use of the method. Several other analytical techniques have also been used for the analysis of this element. Hydride generation atomic absorption spectrometry (HGAAS) is capable of detecting hydride forming arsenic compounds.[5] Most marine samples, which contain non-hydride forming arsenicals, must be digested prior to their analysis by HGAAS, thus incomplete digestion may lead to low recoveries. Inductively Coupled Plasma-Mass Spectrometry (ICP-MS)[6] is another now widely used technique and is similar to ETAAS in that it only requires sample dissolution prior to analysis. The two techniques differ in relative ease and cost of operation, and the types of interferences encountered.[7–9] Other less sensitive analytical techniques such as Neutron Activation Analysis, and ICP-atomic emission spectroscopy have also been used to determine total arsenic.[10] Even though ETAAS compares very well in terms of performance with all the above techniques, a number of interferences have been reported. These are especially pronounced when analyzing environmental samples.[11–13] In order to overcome these interferences, various modifications to parts of the atomic absorption spectrometer (AAS) have been reported. Platform atomizers[10] and matrix modifiers[15] have been used to overcome chemical interferences. Zeeman or deuterium background correction systems have been used to compensate for molecular absorption or light scattering.[16] The performance characteristics of ETAAS are affected by a wide range of instrumental components and furnace heating conditions. Because of the great variation in experimental parameters it is almost impossible to adopt a set of experimental conditions established for use on one AAS system for the determination of arsenic on a slightly modified AAS. Even conditions recommended for a broad category of samples (*e.g.* biological), may not be optimum for a more specific sample type, *e.g.* oyster tissue, on the same spectrometer.

It is therefore evident that an efficient optimization procedure must be adopted in order to accomplish the accurate determination of arsenic in environmental samples. The majority

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of reports to date have used one-factor-at-a-time optimization procedures.[17,18] This has a number of drawbacks; large numbers of experiments are required and the best conditions may be missed if important interactions exist between experimental parameters.

In this study we have used the Composite Modified Simplex (CMS) optimization method.[19,20] This procedure is capable of delineating the optimum experimental conditions using a small number of experiments. A standard Reference Material (SRM) of marine origin containing certified amounts of arsenic was used. The effects of four experimental parameters; ashing temperature, atomization temperature, modifier concentration, and atomization ramping time, on arsenic absorption were optimized by the CMS method and studied.

EXPERIMENTAL

Instrumentation

An Atomic Absorption Spectrometer (Varian Techtron Model AA 1275) equipped with an arsenic hollow cathode lamp (Spectra AA) operating at 8 mA, a GTA-95 graphite furnace, and a deuterium background corrector were used for the arsenic determinations. The 193.7 nm arsenic resonance line was selected and used with a 1 nm bandwidth. Pyrolytically coated graphite partitioned tubes and argon purge gas were also used.

A commercial microwave oven (Sharp Carousel II) was used to digest samples contained in a Teflon decomposition vessel (Parr Instrument Company, 45 ml).

All the simplex calculations were carried out using the OPTIMA3 computer program.[21] This program was run on several PC/XT and PC/AT compatible IBM microcomputers.

Reagents

A 1000 ppm stock solution of arsenic, as arsenic trioxide, was used to prepare all arsenic standard solutions. A 1000 ppm palladium solution, the matrix modifier, was also prepared, this was done by dissolving the appropriate amount of Pd powder in the minimum amount of *aqua regia* followed by dilution with water containing 2% citric acid to the required volume.

Standard solutions containing 100 ppm of arsenic as arsenobetaine, arsenocholine and tetramethylarsonium iodide were also used. These compounds were synthesized by literature methods.[22–24] Microelemental analysis and nuclear magnetic resonance spectroscopy were used to confirm their purity.

Sample solutions were of microwave digested oyster tissue. The freeze dried oyster tissue, standard reference material 1566a, was obtained from the National Institute of Standards and Technology (NIST).

Sample preparation

Samples of 150–200 mg each were weighed directly into the digestion vessel and 2 ml of concentrated nitric acid was added. The digestion vessel was assembled and placed in the microwave oven. The microwave program consisted of one 90 sec step at high power output (500 W).

After cooling the digestion vessel the contents were diluted to 50 ml with de-ionized water. Blanks and arsenic standards were also prepared by using 2 ml of nitric acid and the same digestion and dilution procedure.

Optimization procedure

The simplex optimization was carried out as follows. Four variables were studied for their effect on arsenic absorbance; ashing temperature, atomization temperature, modifier concentration, and atomization ramping time. The experimental variable names were entered into the microcomputer together with their ranges and the precision required for each variable (Table 1). The initial set of conditions was entered and the program then generated the four other sets needed to form the initial simplex and printed worksheets for each experiment. After the completion of the experiments, the actual variable values used and the peak area absorbance were entered. The actual variable values used were kept as close as possible to those suggested by the program.

The program then calculated the next single set of conditions to be investigated and printed another worksheet. This process was continued, the program giving one new experiment each

Table 1. Range and precision of experimental variables examined

Variable	Lower limit	Upper limit	Precision
Ashing temperature (°C)	600	1800	100
Atomization temperature (°C)	1800	2700	100
Modifier concentration (*ppm*)	25	500	25
Ramp time (*sec*)	0.5	8	0.5

time. For each set of conditions three replicates were analyzed by ETAAS. Between each one a blank injection was made to correct for possible lamp drift and also assure that stable repeatable analytical results could be obtained.

The optimum conditions obtained from this procedure were then used to run standard arsenic solutions and quantify the arsenic present in the microwave digested oyster tissue. These conditions were also used to analyze de-ionized water solutions containing arsenobetaine, arsenocholine and tetramethylarsonium iodide.

RESULTS AND DISCUSSION

Various problems have been encountered when analyzing arsenic by using ETAAS, some of which are volatilization losses, interaction with the graphite tube, vapour phase interferences, and spectral interferences.[8,9] Furthermore the analysis of arsenic especially in samples of marine origin may pose additional problems. It is well documented that a large number of arsenic compounds are present in marine organisms.[1] Therefore if the appropriate experimental conditions are not selected it is possible that each arsenical may behave in a different way during ETAAS analysis. This results in sensitivity variations for different arsenicals (due to incomplete detection) and therefore leads to results highly dependent on the arsenic species present. These species dependent effects may be missed if only standard arsenic solutions of artificial origin are used. Consequently it is necessary to optimize the ETAAS conditions using "real" samples. SRMs, which have a similar matrix to the environmental samples of interest, are ideal for the optimization and validation of the method.

NIST oyster tissue was used in this study. Table 2 shows the optimization experiments performed and the responses obtained. Twenty three experiments were required before establishing optimum conditions for the analysis of arsenic in oyster tissue. A total of 33 experiments were performed before ending the optimization search. The recorded absorbance from each experiment as a function of variable value are displayed in Fig. 1.

The optimization procedure very quickly predicted the optimum ramping time. This was 0.5 sec (the minimum limit used in our optimization) and was reached after 13 experiments. Instrumental limitations did not permit use of a shorter ramping time. These results indicate that shorter atomization ramping times improve the arsenic absorbance obtained in ETAAS. Longer ramping times probably allow for loss of arsenic at temperatures close to the atomization temperature.

Table 2. Simplex experiments and ETAAS response

Expt. No.	Cycle*	Abs. (*a.u.*)	[Pd] (*ppm*)	Ashing (°C)	Atomization (°C)	Ramp. (*sec*)
1	0I	0.018	200	700	2000	4
2		0.019	200	1300	2000	4
3		0.015	200	1000	2400	4
4		0.010	200	1000	2100	7
5		0.016	500	1000	2100	5
6	1R	0.025	350	1200	2000	1.5
7	E	0.021	400	1300	2000	0.5
8	2R	0.000	500	1200	1800	1.5
9	C	0.026	300	1100	2200	1.5
10	3R	0.010	50	1200	2100	0.5
11	C	0.018	450	1000	2100	3.5
12	F	0.021	400	1100	2100	3.0
13	4R	0.042	450	1600	2200	0.5
14	E	0.031	500	1800	2400	0.5
15	F	0.038	400	1500	2200	0.5
16	5R	0.029	500	1600	2300	0.5
17	6R	0.030	450	1800	2300	0.5
18	7R	0.032	500	1800	2500	0.5
19	8R	0.037	500	1800	2300	0.5
20	9R	0.028	400	1800	2200	0.5
21	C	0.037	500	1600	2300	0.5
22	F	0.035	450	1700	2300	0.5
23	10R	0.049	500	1500	2200	0.5
24	E	0.040	500	1400	2200	0.5
25	F	0.031	500	1600	2300	0.5
26	11R	0.026	500	1300	2000	0.5
27	C	0.030	500	1700	2400	0.5
28	12R	0.027	500	1300	2200	0.5
29	E	0.038	500	1700	2300	0.5
30	13R	0.045	500	1600	2200	0.5
31	14R	0.041	500	1300	2100	0.5
32	15R	0.040	500	1300	2100	0.5
33	E	0.038	500	1400	2100	0.5

*I: Initial cycle, R: reflection, E: expansion, C: contraction, F: Fit.

Sample standard deviation of 10 blank determinations: 0.002 a.u.

The optimum ashing temperature established in this study was 1500°C. This temperature allows for the removal of matrix components which may otherwise act as interferences for the analysis of arsenic. Higher temperatures result in arsenic loss during the ashing stage, while lower temperatures may result in incomplete removal of various matrix interferences.

The optimum atomization temperature established was 2200°C. We have shown that this temperature allows for complete atomization of all arsenic in the SRM analyzed.

The optimum modifier concentration was 500 ppm (upper limit value). It is our experience that modifier concentrations are not very critical when analyzing standard arsenic solutions, but

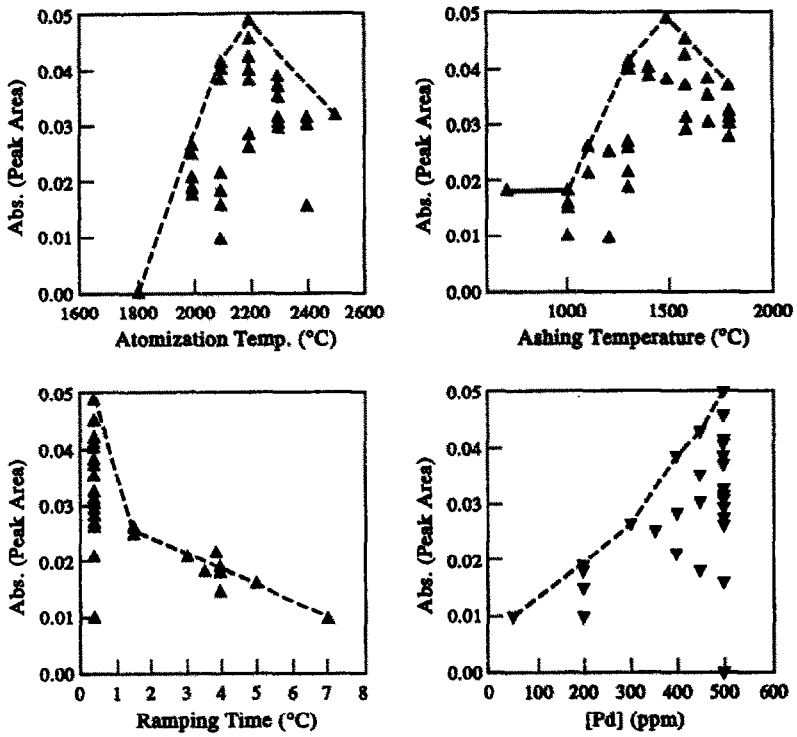

Fig. 1. The absorbances obtained from 33 optimization experiments plotted as a function of the four experimental parameters studied. Dotted lines indicate the estimated highest response level obtained at this value of experimental parameter, irrespective of the values of the other three parameters.

are extremely critical when analyzing environmental samples. This we believe is a consequence of the sample's matrix. In environmental samples palladium may interact with various matrix components and thus be only partially available to act as a matrix modifier for arsenic, thus higher concentrations are required. Use of higher concentration values of Pd results in higher costs per analysis.

The optimum furnace operating conditions along with the solution volumes used in this study are given in Table 3.

Table 3. Furnace heating programme*

Step no.: purpose	Temperature (°C)	Time (sec)	Argon flow (ml/min)
1: Drying	85	5.0	3
2: Drying	95	40	3
3: Drying	120	10	3
4: Ashing	ramp to 1500	5.0	3
5: Ashing	1500	1.0	3
6: Ashing	1500	2.0	3
7: Atomization	ramp to 2200	0.5	0†
8: Atomization	2200	2.0	0†
9: Atomization	2200	2.0	3
10: Clean	ramp to 2600	0.5	3

*Sample and matrix modifier solutions (20 μl of each) injected onto ETAAS.
†Absorbance measured.
Underlined parameters were optimized.

To check if these conditions also resulted in optimum arsenic recovery, the normal calibration method was used to determine arsenic in the NIST standard. The standard additions method was not required. Three samples were microwave digested and analyzed for arsenic, under the optimum ETAAS conditions. The arsenic recovery results obtained from these experiments, in addition to the certified values of arsenic in the SRM, are displayed in Table 4. These results indicate that the experimental conditions allow for quantitative determination of arsenic in NIST oyster tissue.

Because a number of arsenic species, most of which exhibit different physical and chemical properties, have been reported to exist in the environment and in digests or extracts of environmental samples, the ETAAS conditions must be set so that the sensitivity for all these compounds is equal. In order to evaluate if the established optimum conditions resulted in equal sensitivity for different arsenicals, standard solutions of arsenobetaine, arsenocholine

Table 4. Arsenic concentration found in NIST oyster tissue

	Analyzed by ETAAS	Certified value
[As], μg/g	14.5, 14.8, 13.9	14.0 ± 1.2

Table 5. Arsenic concentration of solutions containing organoarsenicals

Compound	[As], μg/mL ETAAS	ICP-MS
Arsenobetaine	0.065 ± 0.003	0.069 ± 0.003
Arsenocholine	0.054 ± 0.002	0.058 ± 0.003
Tetramethylarsonium iodide	0.050 ± 0.001	0.050 ± 0.003

± Sample standard deviation, $n = 3$.

and the tetramethylarsonium ion, were analyzed. These compounds were selected because of their presence in marine organisms. Their determination using ETAAS was investigated by using the optimized experimental conditions previously established. ICP-MS analysis was also performed on these solutions for comparison purposes (Table 5). Data from the table indicate excellent arsenic recovery for the three arsenicals analyzed.

CONCLUSIONS

The application of an optimization procedure such as simplex (in this case the CMS method) in conjunction with a SRM, is of particular value when it is necessary to determine concentrations of a metal or a metalloid such as arsenic in environmental samples. Optimum conditions for various sample matrices can be quickly reached, thus eliminating matrix effects and also sensitivity variations resulting from the different arsenic species present in a particular sample.

This optimization procedure may also be used to improve the analysis of arsenic in the presence of various reagents or buffers used in HPLC eluents, *e.g.* ion-pair reagents such as heptanesulfonic acid.

Recently a number of reports have been published on the analysis of arsenic by using ETAAS in conjunction with mixed modifiers, *e.g.* palladium and magnesium.[25] The procedure used here would be ideal for optimizing the concentrations of these modifiers in conjunction with the appropriate furnace heating program.

We believe that the optimization procedure used here can easily be applied to intelligent automated ETAAS optimization. Since most ETAA spectrometers can be programmed, the addition of simplex optimization is feasible. This would then allow for the optimal analysis of a great variety of environmental samples without any great knowledge about the sample matrix and its effect on arsenic absorption.

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