Research Note

Electrodeposition Techniques for Interference Control in Electrothermal Atomic Absorption Spectrometry

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In this paper, the electrodeposition technique has been studied and developed for in situ separation of analytes from their matrices. This provides the direct determination of trace elements in environmental and biological samples by electrothermal atomic absorption spectrometry. The technique incorporates several steps; a chemico-physical modification is provided first by precoating the graphite furnace with electrodeposited Pd prior to each analysis. The separation of analyte from matrix follows. This is achieved by electrodepositing analyte in situ on the Pd/C surface of the furnace and withdrawing the interfering matrix solution, via the autosampler, before atomisation. Binding to Pd significantly stabilised the volatile elements Pb and Cd and countered retention problems of refractory elements such as Cr, Co and Ni. With a Pd protected pyrolytic graphite surface (under optimized deposition voltage) the analytical performance remains constant and no perceptible changes to the furnace surface condition were observed even after 300-400 firings. The characteristic masses in determination of Pb, Cd, Cr, Co, Ni and Mn in matrices as diverse as dilute acids and 0.1-0.5 M NaCl remain constant, even in some instances without background correction. The detection limits for the above elements have been improved significantly (2-4 fold over the conventional ETAAS) with precision of determination in the range of 2-4 %RSD. Typical calibration graphs for these elements were linear up to 50 μg/l, dependent on the element and matrix.

INTRODUCTION

From all of the reviews and discussions in literature it could be concluded that in the past and still is in the present it could be concluded that the determination of trace elements in complex matrix samples was the important and main problem in the technology, biology, environmental protection, medicine and other fields of science.

Therefore, this work is focused on the study and development of the methods of modification of electrothermal vaporisation and atomization in atomic spectroscopy, particularly in atomic absorption spectroscopy, which is proved to be one of the most sensitive techniques in trace element analysis and the removal of interferences in this technique.

Many studies have reported the use of different techniques for electrolytic preconcentration and sepa-

ration of trace metals from complex matrices in order to eliminate interferences and to improve the limits of detection [1-11].

Between 1980-1984, palladium was found to be a very powerful modifier for determination of mostly volatile elements, and recommended as a universal modifier for graphite furnace (GFAAS) [12-23].

The combination of chemical modification and electrodeposition techniques, with electrothermal atomization in atomic spectroscopy in the proposed techniques shows a better prospect of complete removal of interferences in determination of trace elements even in high concentration of interferent concomitant.

EXPERIMENTAL

The major aim of this work is to develop electrodeposition techniques for in situ separation of analyte from the interferences and preconcentration prior to atomization. This provides the requirements needed to achieve sufficient sensitivity and selectivity to de-

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termine the trace component in the presence of other substances in concentration of several order of magnitude higher.

Procedure

The main part of this work is concerned with using both a chemical modifier and in situ electrodeposition of analyte onto the graphite furnace atomiser, by considering a simple uncontrolled potential electrolysis technique. Pd is reduced in a pre-electrolysing process and pre-coated on the graphite surface. It acts as a chemical modifier for stabilising the analyte in thermal pretreatment programme in the furnace, and as an electrode surface catalyst to help the electrodeposition of analyte on the graphite furnace in the subsequent process. The analyte is separated and deposited as a metallic film onto the inside surface of a pyrolytic graphite furnace tube, that is considered as a negative electrode in these experiments. The spent electrolyte, containing most of the high concentrated concomitants, is removed by autosampler from the furnace. The deposited analyte at this stage could be free from the interferences in the matrix and is in sufficient concentration for determination by ETAAS or any other techniques of atomic spectroscopy.

The autosampler probe-tip is programmed to serve as both a working electrode and a device for introducing the sample into the furnace and removing the spent electrolyte.

Instrumentation

A GBC 932AA double beam atomic absorption spectrometer with deutrium lamp background correction, equipped with GF3000 furnace and PAL3000 autosampler was used through out this work. The instrument and all the accessories were controlled by an external PC, using the GBC Scientific 906 Electrodeposition Software. The autosampler was modified by replacing the last part of the PTFE sample delivery tube by a 6 cm Pt/Ir tube. The furnace and Pt/Ir tube were connected to a d.c. power supply (0-12 V) via a multimeter (0-150 mA) indicating the deposition current.

RESULTS AND DISCUSSION

Electrochemical Pretreatment by Pd Electrodeposition Prior to Sample Introduction

To elucidate the stabilizing effects of Pd on the volatile elements such as Pb and Cd and counter the problem of retention in the furnace for more refractory elements such as Co, Ni, Mn and Cr, a range of experiments was carried out. Detailed results obtained at the maximum applicable pyrolysis temperatures for a loss-free thermal pretreatment are given in Table 1. As is shown in Figure 1, there is practically a total volatilization loss of Cd after pyrolysis at 900°C in the absence of modifier, because cadmium is a very volatile element. However, a full recovery occurs for thermal pretreatment at 600°C and atomization from the furnace precoated with electrodeposited Pd, compared with 80% loss observed without Pd use. The temporal separation of analyte signal from background is another beneficial effect of Pd modifier, providing the possibility of reducing the background absorption by a proper thermal pretreatment.

Separation of traces of Pb from NaCl residual background absorption is shown in Figure 2 after electrodepositing the analyte onto a Pd-coated pyrolytic graphite surface. With nearly complete separation of the analyte from background, using the peak-height mode, the measurement could be carried out without

Table 1. Maximum pyrolysis temperatures for loss-free thermal pretreatment.

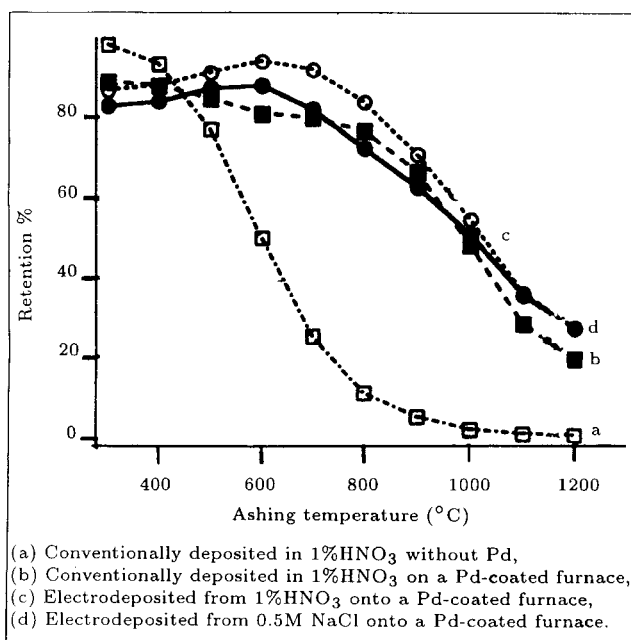| Element	Conven. Inject. Without Pd	Conven. Inject. Pd-Coated	Electrodeposition Pd-Coated from Ammonia Buffer	Electrodeposition Pd-Coated from 0.1 M Nacl
Cd	300	500	600*	600*
Pb	800	1000	1100*	1300**
Co	1000	1000	1000	1200
Cr	1200	1000	1200 Cr(III)# 1200 Cr(VI)#	1200#
Ni	1100	1000	1100	1300
Mn	1100	1100	1100	1200+ 1300++

*) From 1% HNO_3,   **) From 0.5 M NaCl,   #) From 0.02% H_2SO_4,

+) Cathodic deposition as Mn(II)$\rightarrow$Mn,   ++) Anodic deposition as Mn(II)$\rightarrow$MnO$_2$.

(a) Conventionally deposited in 1%HNO₃ without Pd,
(b) Conventionally deposited in 1%HNO₃ on a Pd-coated furnace,
(c) Electrodeposited from 1%HNO₃ onto a Pd-coated furnace,
(d) Electrodeposited from 0.5M NaCl onto a Pd-coated furnace.

Figure 1. Ashing loss curves, measured at Cd 228.8 nm for 0.12 ng Cd.
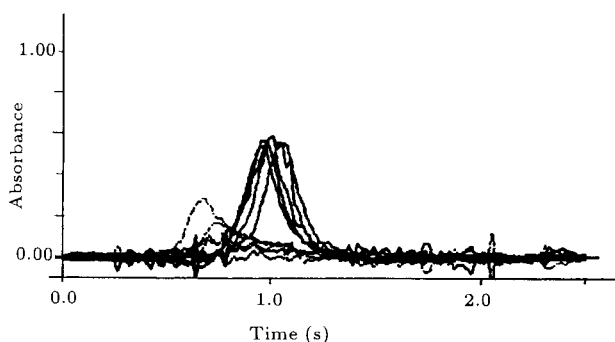
Figure 2. Typical AA (-) and background (...) signals measured at Pb 283.3 nm for 0.5 ng Pb electrodeposited from 0.5 M NaCl onto a Pd-coated furnace.

background correction with an insignificant effect on the accuracy in the interferent concentration range studied. Besides the thermal stabilization of volatile elements, another aspect of Pd layer coating could be related to impregnation of the graphite tube surface. Enhancing the direct contact of analyte with graphite, as well as shielding the active sites to reduce the carbon-analyte interaction, is of special importance when carbide forming elements are determined. In addition to the improved performance of the Pd-coated graphite surface, a relatively long useful lifetime was achieved under optimized parameters for electrodeposition of Pd and analyte. A constant analytical performance with no perceptible change to the surface condition of Pd-coated graphite was observed with aggressive matrix such as 0.5 M NaCl for electrodeposited traces of Pd and Cd up to 350-400 firing (3%RSD). The exfolation of pyrolytic graphite surface

with no Pd coating is reported in literature [14] after 74 determinations for electrodeposition of Pb in this matrix.

Analytical Performance

A primary aim of the search for a new analytical method should be an improvement in sensitivity and/or efficiency with which samples can be analyzed. It is essential to show figures of merit providing the maximum possible assistance in deciding whether the method is likely to be of value for practical analysis. The criteria (figures of merit) used in the selection of a trace analytical method are precision, sensitivity, limit of detection and accuracy. These parameters are called "performance characteristics". The performance characteristics of an analytical method used under a given set of experimental conditions are in fact a set of quantitative and experimentally determined values for parameters of fundamental importance in assessing the suitability of the method for any given purpose. The figures of merit for ED-ETAAS techniques are shown in Tables 2 to 5.

Table 2 compares conventional and ED-ETAAS results obtained for characteristic masses m_0 (criteria to show the sensitivity in ETAAS) of Pb, Cd, Cr, Ni, Co and Mn in a range of matrices. The agreement observed regarding m_0 for different techniques and matrices is quite remarkable. The notable recovery of analyte in an interferent matrix such as concentrated NaCl, without much losses during the high ashing temperature process, shows the capability of this technique for trace analysis in complex samples. This is evident when the results of measurements in complex matrices, by this technique, are compared with those from interference free samples.

In Table 3, Detection Limits (DLs) for the measurement of Pb, Cd, Cr, Ni, Co and Mn by conventional ETAAS are compared with those by ED-ETAAS in different matrices. The results show that for most of the elements, ED-ETAAS has lower DLs than conventional ETAAS in exactly the same experimental conditions. The deposition of Pb and Cd onto the Pd-coated furnace from the same solution, as is used in conventional injection, shows a lower DL. This can be ascribed to improvement in the analyte signal due to bonding to the deposited Pd and delaying analyte release at appearance temperature. This is more crucial when the analyzed solution is 0.5 M NaCl, for which the conventional introduction shows such a high background signal that detection of these elements (Pb and Cd), even at higher concentrations, is impossible. However, in ED-ETAAS, because the analyte is separated by deposition onto the Pd-coated furnace and the interference matrix is removed from the furnace, the DL is even better than that for conven-

Table 2. Comparison of characteristic masses (m_0) for measurements of the elements by conventional ETAAS with electrodeposition (ED)-ETAAS from different matrices, m_0= (sample Vol/μl)(sample Conc./pg/μl)$\times$0.0044/A.

Element	m_0 for Conventional ETAAS from Dilute Acid pg		m_0 for ED-ETAAS from Dilute Acid pg	m_0 for ED-ETAAS from 0.1-0.5 M NaCl pg
	in Inst. Manual	Experiment	Exp.	Exp.
Pb	5.5	6.25	6.19*	6.3**
Cd	0.25	0.48	0.44 − 0.49*	0.49**
Cr	1.5	1.4	1.55 (Cr^{+3})⋆	1.65 (Cr^{+3}) 1.58 (Cr^{+6})
Ni	5	6.3	5.6#	5.6
Co	4.0	3.9	4.2#	4.3
Mn	0.7	0.95	1.05 (anod.)† 0.77 (cathod.)†	1.03 (anod.) 0.74 (cathod.)

* 1% HNO_3, **0.5 M NaCl, ⋆ 0.01% H_2SO_4, # Ammonia buffer solution pH=10, † Ammonia buffer solution pH=4.

Table 3. Comparison of detection limits (D.L.) for measurements of the elements by conventional ETAAS with electrodeposition (ED)-ETAAS from different matrices, (DL=3(SD)$_b$/m)*.

Element	D.L. for Conventional ETAAS from Dilute Acid μg/l$\times$10^{-2}	D.L. for ED-ETAAS from Dilute Acid μg/l$\times$10^{-2}	D.L. for ED-ETAAS from 0.1-0.5 M NaCl μg/l$\times$10^{-2}
Pb	1.65	1.35	1.20
Cd	2.28	0.72	0.45
Cr	2.1	0.3	0.3
Ni	0.63	0.96	0.62
Co	1.29	0.66	1.05
Mn	3.6	1.95 (anod.) 0.69 (cathod.)	1.59 (anod.) 1.26 (cathod.)

* (SD)$_b$ is standard deviation of blank determination, m is slope of standard calibration curve.

Table 4. Precision of measurements for Pb, Cd, Cr, Ni, Co and Mn by ED-ETAAS.

Replicates	Pb A	Cd A	Cr^{6+} A	Cr^{3+} A	Ni A	Co A	Mn* A.s	Mn** A.s	Mn† A	Mn†† A
1	0.522	0.660	0.783	0.637	0.443	0.630	0.397	0.525	0.821	1.05
2	0.520	0.685	0.772	0.637	0.440	0.628	0.386	0.515	0.744	1.04
3	0.517	0.650	0.789	0.636	0.450	0.632	0.395	0.522	0.767	0.936
4	0.524	0.692	0.780	0.640	0.468	0.618	0.385	0.520	0.801	0.936
5	0.506	0.693	0.781	0.635	0.446	0.620	0.391	0.522	0.750	1.04
6	0.514	0.667	0.778	0.642	0.470	0.625	0.388	0.518	0.810	0.942
7	0.506	0.670	0.784	0.638	0.454	0.630	0.393	0.520	0.782	1.03
$\bar{X}$	0.515	0.674	0.781	0.637	0.450	0.625	0.390	0.520	0.782	0.996
%RSD	1.4	2.4	0.7	0.4	2.3	0.8	1.1	0.7	3.5	5.1

A) Peak height absorbance,

A.s) Peak area absorbance,

*) Cathodic deposition ($Mn^{2+} \rightarrow Mn$) from ammonia-sulfuric acid solution (pH = 4),

**) Cathodic deposition ($Mn^{2+} \rightarrow Mn$) from a urine sample,

†) Anodic deposition ($Mn^{2+} \rightarrow MnO_2$) from ammonia-sulfuric acid solution (pH = 8),

††) Anodic deposition ($Mn^{2+} \rightarrow MnO_2$) from ammonia-sulfuric acid solution (pH = 4).

Table 5. Comparison of reproducibility (%RSD) for measurements* by conventional ETAAS and by ED-ETAAS from different matrices.

Element	%RSD Conventional ETAAS in Dilute Acid ($n = 7$)	%RSD ED-ETAAS from Dilute Acid ($n = 7$)	%RSD ED-ETAAS from 0.5 M NaCl ($n = 7$)
Pb	2.0-3.3[†]	1.5-2.4[†]	1.2-2.0
Cd	3.3[††]	3.7[†]	2.5-3.0
Cr	4.9[††]	1.1(Cr^{3+})[††] 2.0(Cr^{3+})[††]	2.4(Cr^{3+})* 4.1(Cr^{3+})*
Ni	2.2[‡]	2.1[‡]	2.3*
Co	4.9[‡]	4.5[‡]	3.6**
Mn	3.8[‡]	4.0 (anod.)[‡] 2.1 (cathod.)[‡]	1.4 (anod.)** 1.0-4.0 (cathod.)**

[†]) 1% HNO_3,   [††]) 0.01% H_2SO_4,   *) 0.1 M NaCl,   **) Urine sample,

[‡]) Ammonia buffer, (anod.) anodic deposition; (cathod.) cathodic deposition,

*) 10 measurement of 7 replicates were made at different times.

tional introduction in an interference free matrix. This highlights the considerable potential of this technique. This conclusion is also valid for the other elements studied. The improvement of DL for carbide forming elements such as Cr is because of the deactivation of the active sites on the graphite furnace by the Pd coating and inhibition of the formation of refractory carbides by this element. The ED-ETAAS technique was also evaluated for precision by measuring Pb, Cd, Cr, Ni, Co and Mn in different matrices. The results of measurements of peak height and peak area for each group of replicates are shown in Table 4 together with %RSD calculated for each group of replicates. As the peak area absorbance showed a better reproducibility for Mn measurements than the peak height absorbance, the former is listed in this table for the element. The calculated %RSD for measurement of Pb, Cd, Cr, Ni, Co and Mn is shown in Table 5 comparing precision of ED-ETAAS from different matrices for these elements with conventional ETAAS.

Calibration curves based on both peak height and peak area measurements were obtained for the above elements in different matrices by ED-ETAAS technique. Figure 3 shows a typical calibration curve for deposition of Pb from 0.5 M NaCl solution prior to measurement by ETAAS. Very good linearity was observed for the elemental concentration ranges of 1-50 ppb, with correlation coefficient better than 0.99 even in a complex matrix of 0.5 M NaCl.

CONCLUSION

From evaluation of the analytical performance of the ED-ETAAS technique presented in this work, it could be concluded that this technique could be considered as a sensitive, precise and accurate one for ultra-
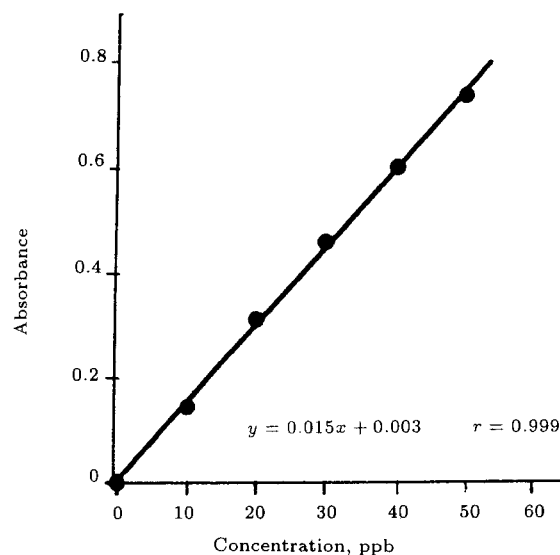
Figure 3. Typical calibration curve for Pb electrodeposited from 0.5 M NaCl onto a Pd-coated furnace at $E_d = 3.0$ V, measured at Pb 283.3 nm (peak height).

trace analysis of most toxic and essential elements in complex matrices of biological and environmental samples.

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