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Development of Hyphenated Techniques with ETAAS for Determination of Ultra-Traces of Manganese and Vanadium and Their Speciation in Environmental Samples

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The technique of in-situ electrodeposition, coupled with ETAAS (ED-ETAAS), has been developed for determination of ultra-traces of manganese and vanadium in environmental samples. The goal is electrodeposition of ultra-traces of analyte onto the renewable Pd-coated substrate at optimized conditions of voltage, time of deposition and pH of sample solution prior to measurement by ETAAS. The characteristic masses in the determination of manganese and vanadium are superior to those of conventional ETAAS (Conv-ETAAS) measurements. The detection limits for the interested elements have been improved over those of Conv-ETAAS, with precision of the determinations in the range of 1-3 RSD%. In this work, a technique was developed for speciation of these elements in the environmental samples. Therefore, a solid phase extraction method, coupled with ETAAS or ED-ETAAS, has been investigated for this purpose. The results showed that it could be a fast and sensitive method for manganese and vanadium speciation. A C_{18} cartridge, modified with sodium diethyldithiocarbamate (SDDTC), has been employed for the selective separation of manganese (VII) ions from other associated metal ions, especially manganese (II), even at much higher concentrations, followed by ED-ETAAS determination. To separate vanadium (IV) from vanadium (V), a modified membrane disk loaded with disodium ethylenediaminetetraacetic acid (Na_2EDTA) was used to trap both vanadium species, then, the vanadium (IV) ion was eluted selectively and ED-ETAAS was used for determination.

INTRODUCTION

Elements such as Mn, Mo, Co, Cr, V, Ni, Se and Sn are considered as essential and Cd, Pb, Hg and As as toxic ultra-trace elements [1]. Adriano [2] defines that the "trace elements refer to the element occurring in the natural and perturbed system in very small amounts and within a narrow margin of concentration which, when present at higher than a specific range of concentration (range of adequacy, specific to each element), is toxic to living organisms". Therefore, sensitive, fast, accurate, simple and reproducible methods have always been required for ultra-trace element analysis.

Electrothermal Atomic Absorption Spectrometry (ETAAS) is one of the mature analytical techniques that is seen as a routine method for elemental analysis in most laboratories. However, the use of this technique is restricted, not only by inadequate sensitivity, but also, by matrix interferences. The direct determination of trace elements in biological or environmental samples by this technique might be difficult because of their low concentration and the complexity of the matrix, which may cause serious interferences. Preconcentration and separation of trace analyte from interfering concomitants could solve these problems and enable sensitive and accurate determination.

The combined electrodeposition and ETAAS technique has proved to be a powerful method to achieve the mentioned requirements for trace element

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analysis of certain metal ions in biological or environmental concerns [3-7]. These papers report the advantages of a combination of both electrolysis and ETAAS techniques to gain reliable results in measuring trace elements in environmental samples. The high sensitivity of these combined techniques is inherently associated with preconcentration and separation by the electrodeposition step. The other aspect of this hyphenated technique is its high potential for elemental speciation [8,9]. The ETAAS cannot usually differentiate between individual species that make up the total element concentration. In contrast, voltametric methods have the necessary potential to differentiate between very labile, moderately labile and inert metal species [10]. Often, it is the simple aqua ion that shows the greatest toxicity, although the lability and stability of the metal complex are key parameters affecting its availability within the diffusion layer of the microorganism's lipid membrane [8]. It is well established that metal speciation is critical to the toxicity of an element and its bioavailability [11-14].

Chemical modification, i.e., changing the thermochemical behavior of both the matrix and the analyte, has also been incorporated as part of the "Stabilized Temperature Platform Furnace (STPF)" in ETAAS measurements [15]. Therefore, the use of modifiers is an essential part of ETAAS to get better control of the complex chemical environment in the furnace. Palladium is one of the most commonly used and powerful modifiers for determination of many elements in ETAAS [16]. It has also been shown that the problem of retention in the furnace for refractory elements, such as, Co, Ni, Mn and Cr, could be countered by an electrodeposited layer of Pd onto the furnace surface prior to injection or electrodeposition of samples [5].

Manganese, at a level higher than the Threshold Limit Value (TLV), has recently been known as a neurotoxin element and the bioavailibility of manganese is of great importance for evaluating the possible health risks to workers. Manganese is an abundant metal, which is widely used in manufacturing steel, welding rods, dry batteries and refractory materials. The workers in these industries are exposed to soluble inorganic manganese compounds and manganese (II) oxides. Chronic Mn overload has shown symptoms of an extrapyramidal system, remarkably similar to those of patients with Parkinson's disease [17]. Judging by the number of papers published in the last few years, there appears to have been a revival of interest in the determination and speciation of this element [10,18,19]. The total manganese is measured mostly by atomic absorption spectrometry [10,20]. The speciation is carried out by voltametric methods [10] or by separation and preconcentration of Mn(VII)/Mn(II) in water samples by adsorption onto crosslinked chitosan, followed by FAAS determination [19]. However, the combined electrodeposition with ETAAS shows superior detection limits by improving characteristic masses for total measurement [5,21]. It has been shown that Mn(II) ions can be quantitatively deposited, both anodically and cathodically, by using the proper applied voltage onto the cell.

Another interested element is vanadium, which is probably considered an essential element. The role of vanadyl ion as an enzyme co-factor and its participation in metabolism, as well as the possibility of its role in the regulation of Na^+/K^+ exchange, have recently been considered [22]. Vanadium is a relatively toxic element for human beings. There is some indication that V(V) as vanadate is more toxic than V(IV) as vanadyl ions [23]. Therefore, it is essential to differentiate V(V) from V(IV) in environmental and biological samples for a better understanding of the toxicity of vanadium. A variety of signs of V toxicity exist because they vary, both with species and with dosage. Some of the disorders provoked by V are gastrointestinal disturbances, depressed growth and cardiovascular disease. Toxicity usually occurs only as a result of high level exposure to airborne vanadium at high concentration [24]. In most previous studies, the total content of vanadium was determined by atomic spectrometry [25-27]. However, the simultaneous speciation determination of V(V)/V(IV) was carried out first by a voltametric technique [28] with very low sensitivity, then, in different pH, the extraction of both species was investigated using chelate resin, in which a lot of sample volume is needed [29,30]. The chromatographic techniques were successfully used for speciation of these ions by using a strong anionic column to trap both vanadium ions then to differentiate them by proper selective elution [23,31].

Therefore, based on the authors' recent work [7], an in-situ micro electrolysis system is developed for preconcentration and separation of ultra-traces of Mn and V from the environmental samples, prior to measurement by ETAAS. The speciation of these elements by the ED-ETAAS technique encountered problems such as showing a very similar reduction potential and the instability of compounds in the condition of deposition.

Some very fast, simple and accurate Solid Phase Extraction (SPE) procedures were developed as a prestep to the ED-ETAAS for speciation of these elements. In these procedures, all species were first trapped onto the modified pre-prepared cartridge or membrane disk, then, selectively eluted by a proper elution process and each species measured by ED-ETAAS after removal.

The application of this hyphenated technique was investigated in environmental samples for the determination and speciation of ultra-traces of Mn and V.

It proves to be a convenient, selective and sensitive technique, which could be available in any laboratory for the above interested detection.

EXPERIMENTAL

Apparatus

A Perkin Elmer model 503 atomic absorption spectrometer, with a deuterium lamp background correction equipped with a HGA-2100 furnace controller, was used throughout this work. All the furnaces were "pyrolytic graphite coated" standard tubes. A 4 cm Pt rod as the anode and the furnace as the cathode were connected to a D.C. power supply (0-12V) via a multimeter (0-100 mA), indicating the deposition current. All of the components are shown, schematically, in Figure 1.

Reagents and Standard Solutions

All reagents were prepared from analytical reagent grade chemicals. De-ionized water from a Mili-Q water system was used. All acids used, namely HCl and HNO_3, were analytically pure. All analyte standard solutions were prepared in 1% v/v HNO_3, by diluting stock solutions of 1000 μg/ml standard solutions of Merck titrasol for AAS.

All the sea, spring and mineral water samples were obtained from the labs in the "Chemical Analysis Research Center, Shahid Beheshti University, Tehran Iran" to be used as real samples. The suspended particulate in the air samples was collected for 8 h, by the handy pump MSA model G, from a vacuum distillation unit and the atmosphere in the Petroleum Refinery Site (in Tehran, Iran), and deposited on a porous filter paper with a diameter of 37 mm and a 0.45 μm pore size from the Millipore company. Then, the filter papers were washed out by dissolving the particulates in 10 ml of 1% HNO_3, to make the sample solutions.

A Metrohom, pH meter model 691 was used for adjusting the pH of the solutions. Empore high-performance disk cartridges, with a 47 mm diameter and 0.5 mm thickness, in combination with standard suction filtration equipment, were used for SPE procedures in the speciation of V(V)/V(IV). For Mn (II)/Mn(VII), in the SPE procedures, the particle loaded membranes (500 mg C_{18} -bonded Silica, 40 μm particle size), prepared from Varian Co., were mounted into standard 6-ml polypropylene syringe barrels, with effective diameters of 10 mm. The membrane disks were about 0.5 mm thick and rested on a support.

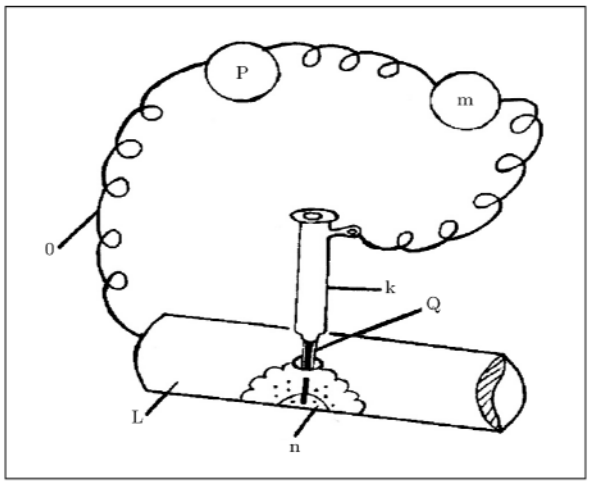

Figure 1. The schematic diagram for the in situ microelectrolysis system in a graphite furnace: m: Multimeter, k: Pt anode, n: Sample drop injected inside the tube, P: Power supply, Q: Glass (Teflon) coating, L: Graphite tube as cathode, O: Connecting wires.

Procedure

Procedures for ED-ETAAS Determination

The experiments involved both conventional and electrodeposition sample introduction into the graphite furnace, coated by an electrodeposited Pd modifier. In the conventional way, a standard furnace program was used to deposit Pd on the tube's surface, prior to sample injection and, then, the sample was injected and the furnace program was run. The deposition of Pd on the tube surface was repeated every cycle. In the ED-ETAAS, following the procedure for Pd electrodeposition and drying of the deposit, 30 μl of the sample (which could be repeated several times for more pre-concentration) or standard solutions were electrolyzed for the specified time period at optimum voltage specific to each element inside the graphite tube. After withdrawing the Pt-electrode from the furnace, the spent electrolytes were removed to separate the deposited elements from the matrix. The deposited metals were dried and a thermal program was run to measure the analyte content.

Procedures for SPE

A 47-mm membrane was placed in a millipore filtration apparatus attached to a water aspirator. For elution, a 200 × 25-mm test tube was placed in the side-arm flask. The disk was washed with acetone to remove any contaminants accumulated from storage, handling or manufacture. It was then conditioned with 10 ml of methanol and 10 ml of deionized water, to promote wetting and uniform flow through the hydrophobic PTFE matrix. Then, the disk was modified, by passing 10 ml of 40 g/l Na_2EDTA solution at a specified rate low enough to capture all the ligands on the disk. Then, a 25 ml sample solution containing V(V) and V(IV) at pH = 6 was sampled at the rate of

1.0 ml/min through the modified disk. Both species were trapped first on the disk and the subsequent selective recovery of V(IV) was achieved by its elution, using 15 ml of an aqueous solution containing: 5 mM Na_2EDTA, tetrabutyl ammonium hydroxide 2 mM and isopropanol 30% at pH = 6. The eluted solution was collected and measured by the ED-ETAAS technique for V(IV) content. V(V) concentration was calculated by subtraction from the ED-ETAAS determinations of the total vanadium content.

The same procedure was used for extraction of Mn(II)/Mn(VII) by a 6 ml syringe disk C_{18} cartridge. After cleaning, the disk was conditioned by passing 10 ml of methanol, 10 ml of 0.1 M HCl, 10 ml of 0.1 $NHNO_3$, 25 ml of deionized water and 10 ml of methanol, respectively, as the system was run under a gentle vacuum. The cartridge was dried by passing through the air for a few minutes. Then, the cartridge disk was modified by coating its surface with a solution of 5 mg of Sodium-Diethyldithiocarbamate (SDDTC) in 0.5 ml of methanol, followed by drying in an oven at 40-50°C. For separation of Mn(II)/Mn(VII) by this modified cartridge, first, 10 ml of the buffer solution (pH = 5, a mixture of 0.1 M HCl and 0.1 M NaOH) was passed, then, 25 ml of solution containing both manganese species were applied in a gentle vacuum. Both species were trapped on the surface of the cartridge and Mn(II) retained by forming the chelate complexes with SDDTC. The subsequent selective elution of Mn(VII) by a solution of HCl 0.1 M was carried out, followed by measurement with the ED-ETAAS technique. The Mn(II) concentration was calculated by subtraction from the ED-ETAAS determinations of the total manganese content.

RESULTS AND DISCUSSION

Measurement and Speciation of Ultra Traces Mn(II)/Mn(VII) by the Combined SPE-ED-ETAAS Technique

It is pointed out in the literature [21] that manganese is the least noble metal, that can be electrodeposited from aqueous solutions on a technical scale. The current efficiency and crystal structure of the electrodeposited manganese are influenced by factors, such as the nature of the substrate, the impurities in the electrolyte, the current density and the temperature. It was also shown that Mn(II) ions can be quantitatively deposited, both anodically and cathodically, at voltages of 1.5-3 V and -2.5-4 V, respectively, applied to the cell. Moreover, in a carefully prepared and purified NH_4Cl-$MnCl_2$ or $(NH_4)_2SO_4$-$MnSO_4$ solution, coarse grained α-manganese was deposited on the platinum, cobalt, nickel and brass electrodes [32].

Referring to the above and to some additional information from the literature [33], ammonium sulfate solutions were selected and used for experiments on the deposition of trace Mn(II) in both forms, by reduction of the metal on the Pd-coated furnace as a cathode, by oxidation to MnO_2 on the Pd-coated furnace operated as an anode and followed by a thermal program for ETAAS measurement. Therefore, The deposition of Mn(II) is performed in two forms:

i) $Mn^{2+} + 2e \xrightarrow{red} Mn$ (cathodically),

ii) $Mn^{2+} + 2\,H_2O \xrightarrow{ox.} MnO_2 + 4H^+ + 4e$ (anodically).

As discussed in detail in previous works [5-7], electrochemical pretreatment by palladium electrodeposition, prior to sample introduction, is carried out in all of these experiments, in order to benefit from the advantages of this Pd layer. Plausible links can be made between the chemical activity of Pd as a catalyst and its chemistry as a modifier. Palladium is also known as an electrocatalyst to be used in the electrolysis process [34]. Besides the catalytic and thermal stabilization properties, another aspect of metallic Pd is related to impregnation of the tube surface, enhancing the contact of analyte with graphite [35]. Due to shielding, the active sites of the carbon-analyte interaction are reduced, which is of special importance when carbide-forming elements are determined. As well as the catalytic properties of the deposited Pd, the furnace surface benefits from its action, due to protecting the furnace against the corrosive and oxidant sample. Therefore, to achieve a renewable, consistent and protected surface for an efficient and rapid analyte deposition, the electrodeposition of Pd onto the graphite surface is essential.

The optimum conditions for electrodeposition of a Pd layer, in regard to efficient and rapid deposition of Mn, were obtained for 30 μl of 40 ppm Pd electrodeposited at an applied voltage of 3.0 V for 50 sec.

Parameters Influencing the Electrodeposition of Mn

Voltage of Deposition

The experimental dependence of the deposition efficiency on the applied voltage for both techniques of cathodic and anodic electrodeposition of manganese from ammonia-sulfate solution buffered to pH = 4, are shown in Figure 2.

In the cathodic electrodeposition, a voltage of at least 4-5 V should be applied to achieve a maximum deposition. At voltages above 7.0, the deposition yield decreased. In the anodic mode deposition, yield was maximal at 2-2.5 V. The yield of deposition decreased at higher voltages between 4-5 V. A plausible explanation for these variations could be the proper oxidation of the Mn(II) ions in the electrolyte solution

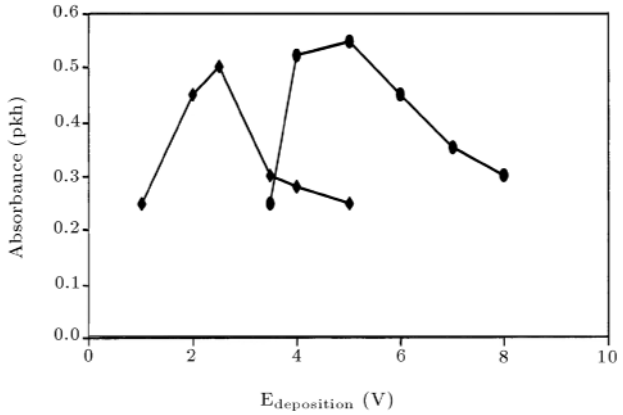

Figure 2. Plots of AA signal versus applied voltage for electrodeposition of 0.15 ng Mn from ammoniacal sulfate solution, both in cathodic (•) and anodic (■) modes, onto Pd-coated furnace at pH = 4.

to Mn(IV) oxides by dissolved oxygen [21], which stir the solution and help the deposition at 2-2.5 V deposition voltage. The low yield observed at lower applied voltage might also arise from the insufficiency of the electrode potential for the deposition process. At more positive voltages, there is a substantial gas evolution and, thus, most of the Mn(II) species have less time to react with dissolved oxygen and to be electerodeposited onto the furnace. It is also possible that the involvement of other species, mainly water, in the electrode process, leads to the evolution of O_2 (in anode) or H_2 (in cathode) gases, which considerably inhibits the deposition of deposits.

Effect of Electrodeposition Time

In Figure 3, the plots of peak-height (pkh) absorbance versus peak height verses time of deposition for both the cathodic and anodic electrodeposition of manganese onto the Pd-coated furnace, are shown.

The deposition was nearly complete for both modes within at least 45 sec. and remained constant for longer depositions, as shown in Figure 2.

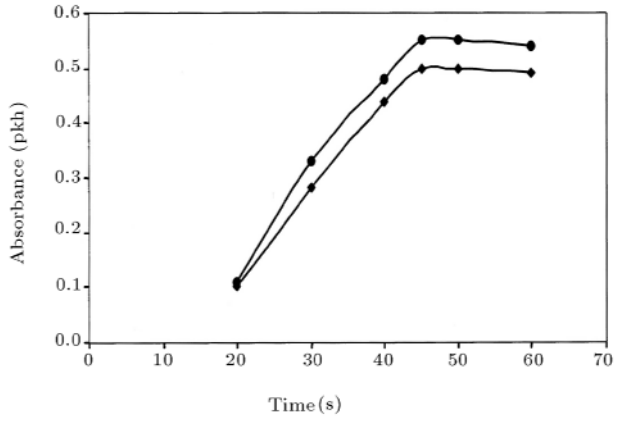

Figure 3. Plots of AA signal versus deposition time for electrodeposition of 0.15 ng Mn from ammoniacal sulfate solution buffered to pH = 4.0, at deposition voltage of 4.0 V, both cathodic (•) and anodic (■) modes, onto a Pd-coated furnace.

Effect of pH on Electrodeposition of Mn

The pH to which the sample is buffered is also very important. It was pointed out by Shiowatana and Matousek [34] that the pH of the sample solution and the applied voltage have an important effect on deposition efficiency, because they influence the degree of hydrogen evolution. As discussed before [5,6], hydrogen evolution could increase the deposition efficiency of metals by contributing to the stirring action, thus, reducing the diffusion layer thickness and improving the efficiency. However, it could also decrease efficiency, by reducing the surface available for metal deposition, particularly at higher deposition voltages.

A number of determinations for cathodic and anodic electrodeposition of traces of manganese were carried out over a range of pH buffered by a buffer solution prior to ETAAS. The results are shown in Figure 4, which demonstrate a marked dependence of deposition in both modes on the pH of the solutions. The higher signals were obtained within the pH region of 3-4.5.

Interesting findings were obtained for the anodic deposition of Mn, as shown in Figure 5.

The double peak for MnO_2, deposited at higher pH traces (Figure 5b) in comparison to a single peak at lower pH traces (Figure 5a), could be an indication of the oxidation of Mn(II) to an oxidation state different from Mn(IV). In this context, Liago [3] discussed the formation of $MnO_n(2 \quad n)H_2O$ from Mn(II) in different solutions, where n depends on the pH of the solutions. In higher pH (about 8.0), the degree of oxidation of Mn is consistent with the product MnO_n, where $n = 1.65$, as shown in that reference.

Therefore, the Mn(II) ions can be efficiently deposited, cathodically, at E_d = 5.0 V, anodically, at

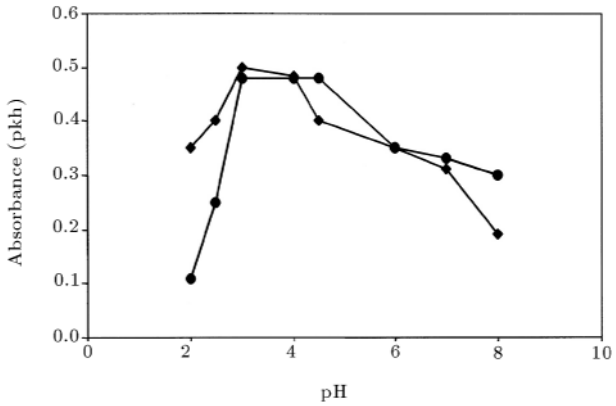

Figure 4. Plots of AA signal versus pH of sample solution for electrodeposition of 0.15 ng Mn from ammonical sulfate solutions, both in cathodic (•) and anodic (■) modes, onto Pd-coated furnace.

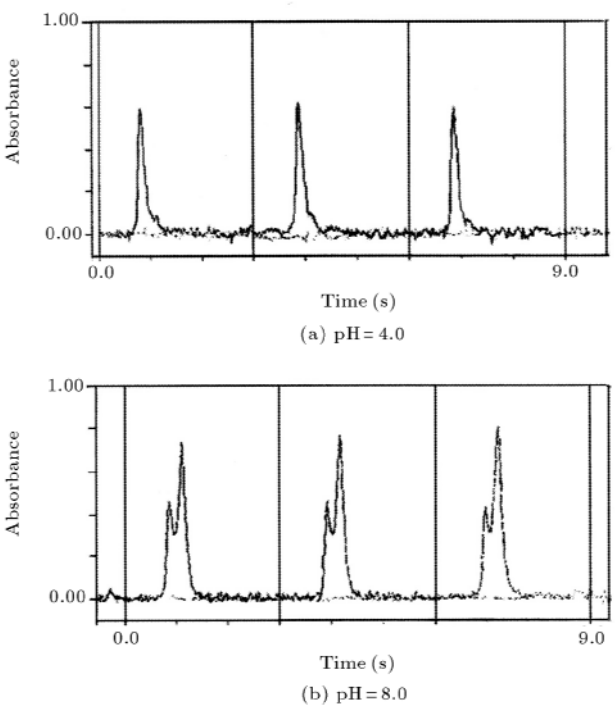

Figure 5. Typical AA (—) and background (- - -) signals measured at Mn 279.5 nm, for anodic electrodeposition of Mn from a buffering ammonical sulfate solution onto a Pd-coated furnace at a) pH = 4.0 and b) pH = 8.0.

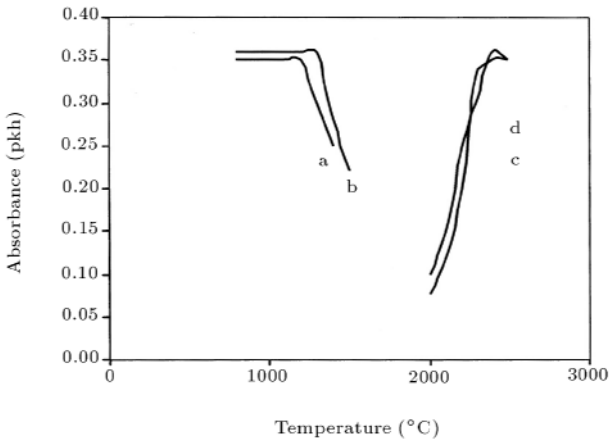

Figure 6. Ashing loss and atomization curves, measured at Mn 279.5 nm for 0.1 ng Mn: a) Ashing loss in conv-ETAAS; b) Ashing loss in ED-ETAAS; c) Atomization plot in conv-ETAAS; and d) Atomization plot in ED-ETAAS.

E_d = 2.5 V within 40 sec and from solutions with a buffered pH of 4.0. Figure 6 demonstrated the ashing and atomization plots in conv-ETAAS and ED-ETAAS (at specified conditions for electrodeposition).

Actually, as Mn is not a volatile element, the Pd-coated furnace has little effect on the pyrolysis characteristics of this element. However, the important action of the modifier, as discussed before, is not so much further increased in thermal stability, but, in the control of the chemical environment. This means that the binding with Pd protected the analyte elements and prevented the formation of any undesirable compounds with the matrix or the active carbon site of the graphite tube. The slight improvements in sensitivity and even in thermal stability, have been observed in the results shown in Figure 6.

Analytical Performance of ED-ETAAS

The limits of detection and characteristic masses for the measurement of Mn by conv-ETAAS are also compared with those by ED-ETAAS. As illustrated in Table 1, the results show an improvement of 20% in LOD for ED-ETAAS in a more complex matrix, compared to that of the conv-ETAAS in the standard solution. This can be ascribed to an improvement in the analyte signal, due to preconcentration, as the result of more effective binding to the furnace surface and delay of analyte release to the time of the higher temperature. The ED-ETAAS technique, because the analyte is separated by deposition onto the Pd-coated furnace from the interfering matrix, also shows an improvement in the slope of the calibration curves and in the characteristic masses for this technique in the measurement of Mn. The slopes of the calibration curve and the measurements of m_o and LOD, for both techniques, are shown in Table 1.

For evaluation of the performance of the ED-ETAAS technique in the measurement of ultra-traces of manganese, the application of this method was tested on real samples. The results are shown in Figure 7. Ultra-traces of analyte added to a sea water sample, deposited under the conditions of electrodeposition specific to catholically deposited Mn, show nearly 100% recovery. The slopes of the analytical curves, for both analyte in an interference-free solution and analyte added to a seawater sample, were the same within experimental error. This indicates the capability of the ED-ETAAS technique to separate the analyte from

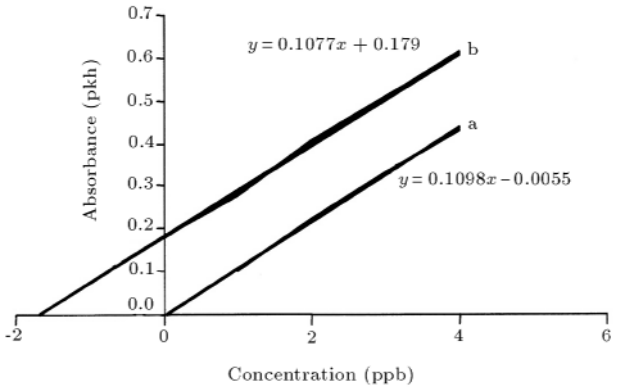

Figure 7. Calibration curves for Mn electrodeposited from: a) Ammoniacal buffer solution; and b) Sea water sample.

Table 1. Comparison of Limit Of Detection (LOD), characteristic mass (m_o) and precision (RSD%) in measurement of 0.15 ng Mn by ED-ETAAS with conv- ETAAS.

	Type of Deposition	m (Slope of Calibration Curve)	m_o^*/ (pg)	LOD**/ (ppb)	RSD% (n = 7)
Conv.-ETAAS	Conventional injection	0.065	0.95	0.34	3.87
ED-ETAAS	Electro-deposition -cathodic[a]	0.1093	0.74	0.29	2.71
	-anodic[b]	0.1056	0.77	0.31	3.00

a) $Mn^{2+}+2e \rightarrow Mn$, from 0.1 M NaCl, b) $Mn^{2+}+2H_2O \rightarrow MnO_2+4H^+ +2e$, from 0.1 M NaCl,

*) $m_o = \frac{(\text{sampleVol.}\mu l)\times\left(\text{sampleconc.}\frac{pg}{\mu l}\right)\times 0.0044}{A}$,

**) DL = $3S_b/m$, S_b is standard deviation for the blank, and m is the calibration curve slope.

Table 2. Recovery test for Mn measurement by ED-ETAAS technique.

Added Stds.	Blank	Sea Water	
Conc./ppb	Abs./pkh	Abs./pkh*	Recovery%
0.0		0.181	
1.0	0.100	0.280	99
2.0	0.220	0.401	100.8
3.0	0.325	0.502	96.1
4.0	0.431	0.608	100

*: pkh: peak-height.

the bulk of the interfering matrix in a sea sample that performs an interference free determination with full recovery of added analytes. The results have been shown in Table 2.

The application of the technique was tested on real samples. The results obtained from the analysis of one urine standard reference sample (SRM 2670), two water samples and two air particulate samples were compared to those reported in the reference certificate and also to those analyzed by the conv-ETAAS technique, by using the same modifier. The data are shown in Table 3. As illustrated in this table, in the very complex sample, such as the urine sample, the conv-ETAAS is unable to measure the Mn content whereas the proposed ED-ETAAS results show a very good agreement with those of certified values. It is also concluded, from this brief evaluation, that the proposed technique is quite promising for the validation of accuracy in measurement by the efficient and complete deposition of the analyte.

Separation and Preconcentration of Mn(II)/Mn(VII) Species by SPE and Determination by ED-ETAAS

As mentioned before, the ED-ETAAS technique has shown a potential ability for speciation of many elements [8,9]. Therefore, it was employed for the Mn ions speciation in environmental samples. Unfortunately,

Table 3. ED-ETAA analysis of NIST urine (SRM2670) and some real samples for Mn content (n = 7).

	Conv-ETAAS	ED-ETAAS Cathodic	ED-ETAAS Anodic	NIST# Certified Value
Sample	**Conc./ppb**	**Conc./ppb**	**Conc./ppb**	**Conc./ppb**
Sea Water	20.9	22.3	22.1	
Spring Water	7.1	7.5	7.3	
Air Particulate*	0.35	0.39	0.37	
Air Particulate**	1.75	1.77	1.76	
Urine Sample (SRM 2670)				
-Normal Level	———	29.2 ± 5.4		(30)
-Elevated Level		310 ± 2.8		(330)***

* Collected from refinery site,

** Collected from vacuum distillation,

NIST: National Institute of Standard and Technology, Gaithersburg, USA,

*** The results shown in brackets are not certified.

reproducible results could not be achieved, which may be due to the reduction of Mn(VII) ions into the different oxidation states of manganese at the cathodic potential.

In this approach, the solid-phase extraction technique has been employed to separate and, furthermore, preconcentrate the Mn(II)/Mn(VII) prior to measurement by ED-ETAAS. The retention of these metal ions is performed, first, by using sodium Diethyldithiocarbamate (SDDTC) as a chelating reagent on the C_{18} cartridges. Then, the aqueous samples are passed through the cartridge. This causes the metal ions in solution to come into intimate contact with a comparatively high concentration of chelating reagent on the resin surfaces. In this method, the contact time is relatively short, so the rate of chelate formation must be rapid. The SDDTC compound is used to form the neutral metal complexes with the Mn ions. Actually, Mn(II) forms a colorless complex of $Mn(DDTC)_2$, which is soluble in organic solvents, but, Mn(VII) could not form any complex with this reagent. Therefore, this difference makes it possible to separate them at the next step. Additional selectivity could be achieved by pH adjusting. The sorbed metal complexes were eluted with a proper solvent for subsequent ED-ETAAS measurement. The results of experiments for finding the proper eluent for selective elution of the ions, on methanol, 0.1 N HCl, 0.1 N H_2SO_4 and 0.1 N HNO_3, showed that $Mn(DDTC)_2$ could be exclusively eluted by methanol and HCl could be eluted only by Mn(VII) ions. As the use of inorganic solvents resulted in a more reproducible and accurate result in ETAAS, the 0.1 N HCl is used for selective elution of the Mn(VII) ions from the membrane.

The Effect of Ligand Concentration

In order to optimize the amount of coated layer of SDDTC on the cartridge surface for achieving the best result for efficient retention of both ions, the experiments were carried out with different amounts of the ligands in the ranges of 2-10 mg dissolved in 0.5 ml methanol. The results showed that over 5 mg ligand is enough, so this amount of ligand was used in all subsequent experiments.

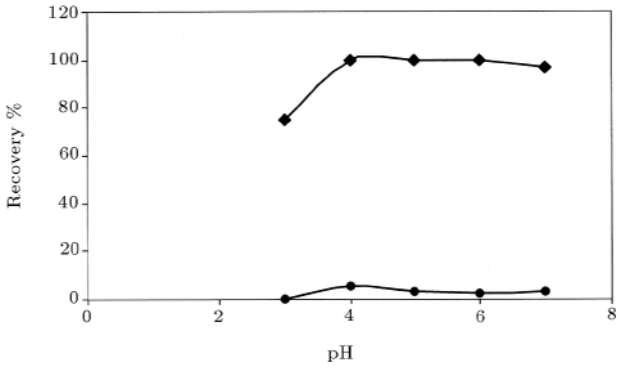

Figure 8. The effect of pH of sample solutions on recovery of 100 ng each of Mn(VII) (♦) and Mn(II) (●).

Effect of pH on % Recovery of Mn(VII)

As discussed before, one of the important factors that affects the efficiency of the speciation in this method is the pH of the solution. The results, shown in Figure 8, illustrate the effect of the pH of the solution on the retention and recovery of these ions. At pH = 5 and over, the recovery of Mn(VII) is nearly 100% and no Mn(II) complexes were eluted by 0.1 M HCl. Therefore, this pH was adjusted for all the sample solutions during the tests.

The effect of interferent ions in the solution was investigated in a series of experiments and no interferences were observed by Na^+, K^+, Ca^{2+}, Mg^{2+}, Cr^{3+}, Fe^{2+}, Zn^{2+}, Co^{2+}, Ni^{2+}, Pb^{2+}, Cl and $SO_4{}^2$ within a specified concentration in the experiments (similar to the matrix of sea water).

Analytical Performance of Combined SPE-ED-ETAAS

In addition to all the capabilities of ED-ETAAS, the prestep SPE made it possible to separate, quantitatively, Mn(VI) ions from solutions up to 400ml onto the modified cartridges. The preconcentration factor was about 80 times more and the LOD was about 0.02 ng/ml.

To evaluate the capability of the technique in the speciation of these two ions in real samples, the recovery tests were carried out on two water samples. The results are shown in Table 4.

The analytical response curves for the increased concentration of both ions in the solution are shown in

Table 4. Measurement and speciation of Mn ions in water samples by SPE-ED-ETAAS.

	Mn Added (pbb)		Mn Found (pbb)		%Recovery	
Sample	**Mn(II)**	**Mn(VII)**	**Mn(II)**	**Mn(VII)**	**Mn(II)**	**Mn(VII)**
Sea Water	0.0	0.0	22.3	0.0	–	–
	1.0	1.0	23.28	1.0	98	100
Spring Water	0.0	0.0	7.5	0.0	–	–
	1.0	1.0	8.46	0.99	96	99

Figure 9. The results were promising for the selective measurement of Mn(VII) ions, even in the presence of higher concentration Mn(II) ions.

Measurement and Speciation of Ultra Traces V(V)/V(IV) Ions by Combined SPE-ED-ETAAS Techniques

The proposed technique was also applied for measurement and speciation of vanadium ions in the environmental samples. The results showed that the quantitative electrodeposition of vanadyl sulfate solutions onto a Pd-coated furnace as a cathode is achieved at optimized conditions specified for this element (5.0 V deposition voltage, from ammonia buffer solution at pH = 8.0, for 60 sec). The ashing and atomization curves for vanadium measured by this technique, in comparison to those of the conventional ETAAS, are shown in Figure 10. The criteria for the analytical performance of ED-ETAAS for vanadium measurements, are also shown in Table 5.

Figure 11 shows the results of spiked vanadium to a mineral water sample.

The slopes of the analytical curves for both analyte in an interference-free solution and analyte added to a mineral water sample, were the same within the experimental error. This indicates the capability of the ED-ETAAS technique for separating the analyte from the bulk of the interfering matrix in a real sample and performs an interference free determination with a full recovery of added analytes.

The SPE-ED-ETAAS technique was also applied for the speciation of V(V)/V(IV) in an environmental sample. The procedures have been described in the previous sections and the results are shown in Table 6.

CONCLUSION

One can conclude from all the results demonstrated in this paper that the combined electrodeposition technique with ETAAS has progressed substantially towards the ultimate goal of the ETAAS, i.e.: direct, interference free, ultra-trace analysis of complex samples, with a remarkable improvement in sensitivity and precision, as well as extending the ability of the technique toward speciation analysis.

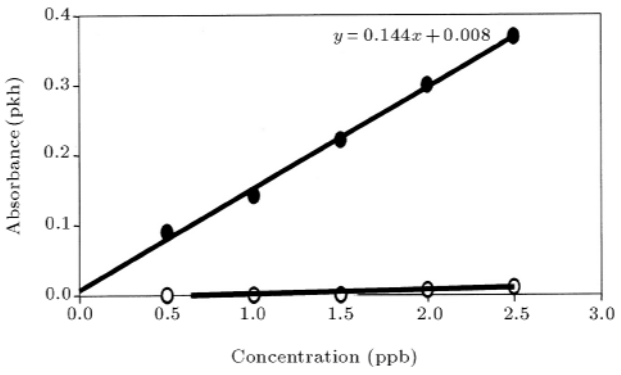

Figure 9. The plots of analytical response curves for Mn measurement by SPE-ED-ETAAS, versus Mn(VII) (•), Mn(II) (∘) ions concentrations.

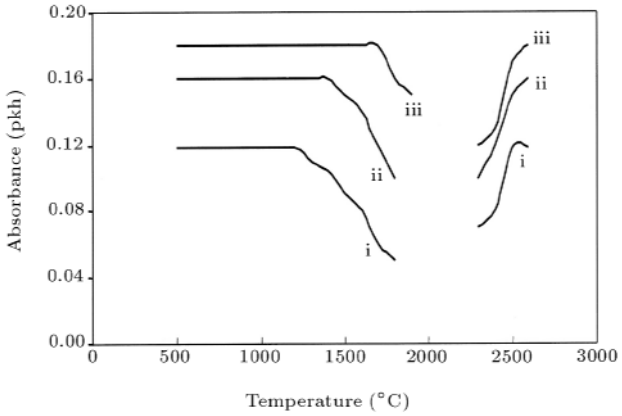

Figure 10. Ashing and atomization curves, measured at vanadium 318.4 nm, i) conv-ETAAS, without Pd coating (1200°C ash. and 2450°C atm.); ii) conv-ETAAS, with Pd-coating (1500°C ash. and 2500°C atm.); and iii) ED-ETAAS, onto Pd-coated furnace (1700°C ash. and 2600°C atm.).

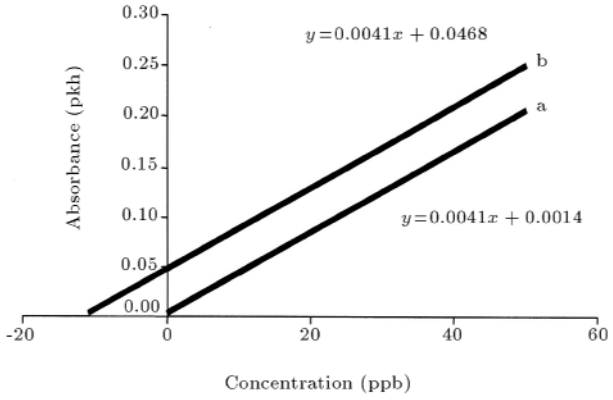

Figure 11. Spiked vanadium to Damavand mineral water, measured by ED-ETAAS.

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Table 5. Analytical performance of ED-ETAAS in measurement of V.

Analytical Merits	Conv-ETAAS	ED-ETAAS
LOD (ppb)	3.00	1.00
m_o **(pg)**	33.00	27.50
% RSD (n = 7)	3.59	2.98

Table 6. Measurement and speciation of V(V)/V(IV) ions in environmental samples by SPE-ED-ETAAS.

Sample	V(IV) (ppb)	V(V) (ppb)
Polour$^+$	22.6	19.9
Damavand$^+$	12.7	15.9
Sabalan$^+$	8.3	2.1
Air Particulate Matter*	< LOD[a]	1.23

+) Mineral water,

*) Collected from refinery site (vacuum distillation),

a) Limit of detection (1 ng/ml).

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