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SIMULTANEOUS DETERMINATION OF METALS AT TRACE LEVEL IN A MULTICOMPONENT SYSTEM. APPLICATION TO REAL SAMPLES†

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Abstract—Voltammetry is a very suitable, versatile and rapid method for the simultaneous metal determination in complex matrices. The present work, regarding the determination of Cu, Fe, Cr, Sn, Ti, Mo and Mn, is a very interesting example of the possibility to determine single elements in real samples. 0.1 M ammonium citrate (pH 6.1 and 8.5) was employed as the supporting electrolytes. Differential pulse voltammetric (DPV) and alternating current voltammetric (ACV) measurements were carried out using, as working electrode, a stationary mercury electrode, as auxiliary a platinum electrode and as reference an Ag/AgCl, KCl sat. electrode. The analytical procedure was verified by the analysis of standard reference materials such as Stainless Steel (AISI 321) NBS-SRM 121d1 and Highly Alloyed Steel Eurostandard 281-1a. Precision and accuracy, expressed as relative standard deviation and relative error, respectively, were of the order of 3–5%, while the detection limit for each element was around 10^{-9} M. The standard addition technique extends the usefulness of the voltammetric method to very high element concentration ratios. Copyright © 1996 Elsevier Science Ltd.

Key words: voltammetry, trace determination, interferences, real samples, alloys.

INTRODUCTION

Multi-element analysis is a goal which must be persued in all analytical methods. In the analysis of metals in real matrices a lot of determinations have been carried out by means of spectroscopic techniques, which unfortunately need several very expensive instruments for simultaneous determination of different metals[1].

It is felt that voltammetric methods can be a valid and effective option in the multicomponent analysis of metals, since a single potential scan in an appropriate supporting electrolyte can give a qualitative and quantitative analysis with good selectivity, employing a simple inexpensive instrumentation.

In particular the high sensitivity of the voltammetric method[2, 3] can be combined with the considerable selectivity, especially if the second harmonic alternating current technique is employed[4–6].

The sensitivity and selectivity have further been improved by the introduction of new types of electrode[7–9] and new quantitative methods based on extrapolation after multiple standard additions[10, 11]. In previous communications[9–12], sensitive and selective voltammetric methods were reported for the simultaneous determination of several elements in real matrices. The present work is the continuation of this line of research. Here, the simultaneous determination of seven elements, Cu, Fe, Cr, Sn, Ti, Mo and Mn, in the alloy matrices stainless steel (AISI 321) NBS-SRM 121d1 and highly alloyed steel Eurostandard 281-1a, is presented.

The above mentioned elements, in matrices of this type, frequently interfere with one another[13]. The method proposed reduces the interferences without compromising the precision, accuracy and speed. These results have been obtained by combining an appropriate supporting electrolyte (0.1 M ammonium citrate pH 6.1 and 8.5) with the standard addition method, applied to the case of very high element concentration ratios.

EXPERIMENTAL

Apparatus

Voltammetric measurements were carried out with an AMEL (Milan, Italy) Model 471 Multipolarograph in conjunction with an AMEL Model 430 polarographic stand. The working electrode was the AMEL polarographic stand operated as a hanging drop mercury electrode, while an Ag/AgCl, KCl sat. electrode and a platinum wire were used as the reference and the auxiliary electrode, respectively. The voltammetric cell was kept at $25.0 \pm 0.5°C$. The solutions were deaerated with pure nitrogen for 15 min prior to the measurements, while a nitrogen blanket was maintained above the solution during the analysis. Standard additions were made with Gilson micropipettes with disposable plastic tips. The solutions were deaerated for 2 min. after each standard addition.

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Table 1. Experimental peak potentials ($-E$, V/Ag, AgCl, KCl sat., ± 0.005). Experimental conditions: see Table 2

| Element | Voltammetric technique | | | |
| | pH = 6.1 | | pH = 8.5 | |
	DPV	ACV	DPV	ACV
Cu	0.165	0.170	0.340	0.345
Fe	0.225	0.225	0.475	0.485
Cr	0.375	0.370	0.190	0.185
Sn	0.605	0.610	0.755	0.750
Ti	0.905	0.915	—	—
Mo	1.010	1.005	1.265	1.255
Mn	1.615	1.615	1.630	1.620

Reagents and reference solutions

All solutions were prepared with deionized water (Millipore, Milli Q), and all reagents were suprapure grade. Aqueous stock solutions of copper, iron, chromium, tin, titanium, molybdenum and manganese were prepared by dilution of the respective standard $1000\,mg/dm^3$ solutions (BDH, England). The Teflon voltammetric cell was rinsed every day with supra-

Table 2. Experimental conditions for the determination of the elements by differential pulse (DPV) and fundamental harmonic alternating current voltammetry (ACV)[a]

	DPV	ACV
E_i	-0.050	-0.050
dE/dt	10	10
f	—	100
ΔE	50	10
Φ	—	$270 + 87$
τ	0.065	—
v	0.250	—

[a] E_i: initial potential (V/Ag, AgCl, KCl sat.); dE/dt: potential scan rate (mV/s); f: frequency (Hz); ΔE: amplitude of alternating current voltage (ACV) and pulse (DPV) superposed (mV); Φ: demodulation phase angle (degrees); τ: pulse duration (s); v: pulse repetition (s).

pure concentrated nitric acid to minimize potential contamination.

Sample preparation

Stainless steel (AISI 321) NBS-SRM 121d1 and highly alloyed steel Eurostandard 281-1a were prepared according to Thomerson and Price[14]. Approximately $0.2–0.3\,g$ of sample, accurately weighed in a platinum crucible, was dissolved by adding $1\,cm^3$ of 37% (m/m) hydrochloric acid and, subsequently, $1\,cm^3$ of 69% (m/m) nitric acid. After the initial reaction had subsided, $2\,cm^3$ of 60% (m/m) perchloric acid was added, and the solution was evaporated until the sample was fully oxidized and fumes of perchloric acid appeared. The solution so obtained was kept at the same temperature for about $5\,min$. After cooling, the soluble salts were dissolved in $25\,cm^3$ of 0.1 M ammonium citrate pH 6.1. Successively, in order to obtain the pH value equal to 8.5, concentrated NH_4OH was carefully added.

RESULTS AND DISCUSSION

The metals determined are the main components of the two alloys stainless steel (AISI 321) NBS-SRM 121d1 and highly alloyed steel Eurostandard 281-1a, that is Cu, Fe, Cr, Sn, Ti, Mo and Mn. In the same matrices Co and Ni are also present. The analytical procedure for their determinations has been reported in a previous paper[15]. It must be considered also the fact that Co and Ni do not give reversible electrodic process in 0.1 M ammonium citrate at pH 6.1 and 8.5, and, for this reason, they do not interfere in the determination of the metals above mentioned.

Aqueous standard reference solutions

Before the analysis of the standard reference materials, a preliminary study was carried out for the determination of each element alone and in the presence of a large excess of interferents. The voltammetric techniques employed were differential pulse

Table 3. Analytical calibration functions of elements in 0.1 M ammonium citrate (pH 6.1) as supporting electrolyte (aqueous reference solutions)[a]

Element	Differential pulse voltammetry	Alternating current voltammetry
Cu	$i_p = (0.02 \pm 0.02) + (3.85 \pm 0.03) \times 10^6\,c$ $r = 0.9991 \quad s_r = 3.4\% \quad DL = 5.19 \times 10^{-9}\,M$[b]	$i_p = (0.01 \pm 0.02) + (2.69 \pm 0.06) \times 10^6\,c$ $r = 0.9990 \quad s_r = 3.8\% \quad DL = 7.43 \times 10^{-9}\,M$
Fe	$i_p = (0.01 \pm 0.02) + (2.99 \pm 0.05) \times 10^6\,c$ $r = 0.9990 \quad s_r = 4.2\% \quad DL = 6.69 \times 10^{-9}\,M$	$i_p = (0.01 \pm 0.01) + (1.43 \pm 0.05) \times 10^6\,c$ $r = 0.9993 \quad s_r = 2.6\% \quad DL = 1.40 \times 10^{-8}\,M$
Cr	$i_p = (0.02 \pm 0.02) + (1.87 \pm 0.06) \times 10^6\,c$ $r = 0.9993 \quad s_r = 2.7\% \quad DL = 1.07 \times 10^{-8}\,M$	$i_p = (0.01 \pm 0.02) + (0.87 \pm 0.06) \times 10^6\,c$ $r = 0.9989 \quad s_r = 3.9\% \quad DL = 2.30 \times 10^{-8}\,M$
Sn	$i_p = (0.01 \pm 0.01) + (2.48 \pm 0.04) \times 10^6\,c$ $r = 0.9991 \quad s_r = 3.9\% \quad DL = 8.06 \times 10^{-9}\,M$	$i_p = (0.02 \pm 0.02) + (1.02 \pm 0.07) \times 10^6\,c$ $r = 0.9990 \quad s_r = 2.8\% \quad DL = 1.96 \times 10^{-8}\,M$
Ti	$i_p = (0.01 \pm 0.02) + (6.52 \pm 0.07) \times 10^5\,c$ $r = 0.9995 \quad s_r = 2.3\% \quad DL = 3.07 \times 10^{-8}\,M$	$i_p = (0.02 \pm 0.03) + (3.06 \pm 0.08) \times 10^5\,c$ $r = 0.9988 \quad s_r = 4.7\% \quad DL = 6.54 \times 10^{-8}\,M$
Mo	$i_p = (0.01 \pm 0.01) + (2.89 \pm 0.05) \times 10^5\,c$ $r = 0.9992 \quad s_r = 3.0\% \quad DL = 6.92 \times 10^{-8}\,M$	$i_p = (0.01 \pm 0.02) + (1.61 \pm 0.08) \times 10^5\,c$ $r = 0.9990 \quad s_r = 3.6\% \quad DL = 1.24 \times 10^{-7}\,M$
Mn	$i_p = (0.02 \pm 0.02) + (2.06 \pm 0.05) \times 10^5\,c$ $r = 0.9989 \quad s_r = 4.8\% \quad DL = 9.71 \times 10^{-8}\,M$	$i_p = (0.02 \pm 0.02) + (1.05 \pm 0.09) \times 10^5\,c$ $r = 0.9989 \quad s_r = 4.3\% \quad DL = 1.90 \times 10^{-7}\,M$

[a] The errors correspond to a probability of 95%; i_p = peak current (μA); c = concentration of the electroactive species (M).

[b] Limit of detection (DL) is expressed according to IUPAC[16] and corresponds to a probability of 99%.