Análisis de metales traza por redisolución anódica con monitoreo potenciométrico redox químico con un sistema de mínima instrumentación.

Minimal instrumentation stripping potentiometric analysis (SPA) of trace metals

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Introduction

Potentiometric stripping analysis (PSA) is an electrochemical method for the determination of metals at low concentrations. A typical PSA analysis is performed in two stages:

a) Deposition step: $M^{n+} + ne^- + x\,Hg^0 \longrightarrow M(Hg^0)_x$

b) Potentiometric stripping step: $M(Hg^0)_x + {}^{n}/_{2}\,Hg^{2+} \longrightarrow M^{n+} + (x+{}^{n}/_{2})\,Hg(l)$

There is a potential imposed by the system along the stripping step with abrupt potential changes in a time, known as transition time.
This parameter is proportional to analyte concentration, allowing quantified an analyte by PSA curves E=f(t). The aim of this work is to describe a PSA system produced with local instrumentation and show calibration plots done with this equipment for the analysis of lead, copper and cadmium.

Experimental work

Lead, cadmium, copper, bismuth and zinc were analyzed by calibration plots at ppm levels. The electrodes used were glassy carbon as working electrode (WE), graphite as auxiliary electrode (AE) and Ag|AgCl$_{(s)}$, KCl sat.|| as reference electrode (RE). The initial step was the preparation of a thin layer mercury electrode (TLME). The deposition step was carried out by setting a -1.5 V vs RE potential over the WE for 4 minutes, then the potentiometric stripping step was recording as an OCP vs t. plot. The media used in each analysis was NaCl 0.5 mol L^{-1}, HCl 0.05 mol L^{-1}, Hg(II) $5x10^{-5}$ mol L^{-1}.
A sample containing the three metallic ions on study was analyzed. In addition, the effect of deposition time over the potentiometric stripping step was tested.
Finally, the method was applied to a real sample of a local alcoholic beverage known as Tonayán, by the standard additions method.

Equipment

Code	Material	Cost (MNX)	Cost (USD)	Cost (EUR)
1	MIMP [4-7]	2000	111.42	97.75
2	Chronometer	100	5.57	4.89
3	Computer	-	-	-
4	Microstirrer	160	8.91	7.82
5	Syringe	5	0.28	0.24
6	Plastic vessel	5	0.28	0.24
7	Ag|AgCl$_{(s)}$, KCl sat.||	100	5.57	4.89
8	Glassy carbon	1500	83.57	73.31
9	Graphite	15	0.84	0.73
10	Microstir bar	150	8.36	7.33
	Total	4035	224.8	197.21

Table 1. Materials cost

Figure 1. Low cost microPSA device

The materials needed for build the device are listed in Table 1. The total cost of the device is 224.8 UDS or 197.2 EUR, which is lower than other analyzers used for low concentration analysis.
The microPSA device is shown in Figure 1.

Results and analysis

Typical PSA curves are shown in Figure 2. PSA curves were performed with Pb(II), Cd(II), Cu(II), Bi(II) and Zn(II), resulting into the calibration plots shown in Figure 3. The properties of the curves, limits of detection (LOD) and quantification (LOQ) are shown in table 2. LODs are below of 1 ppm for all cases.

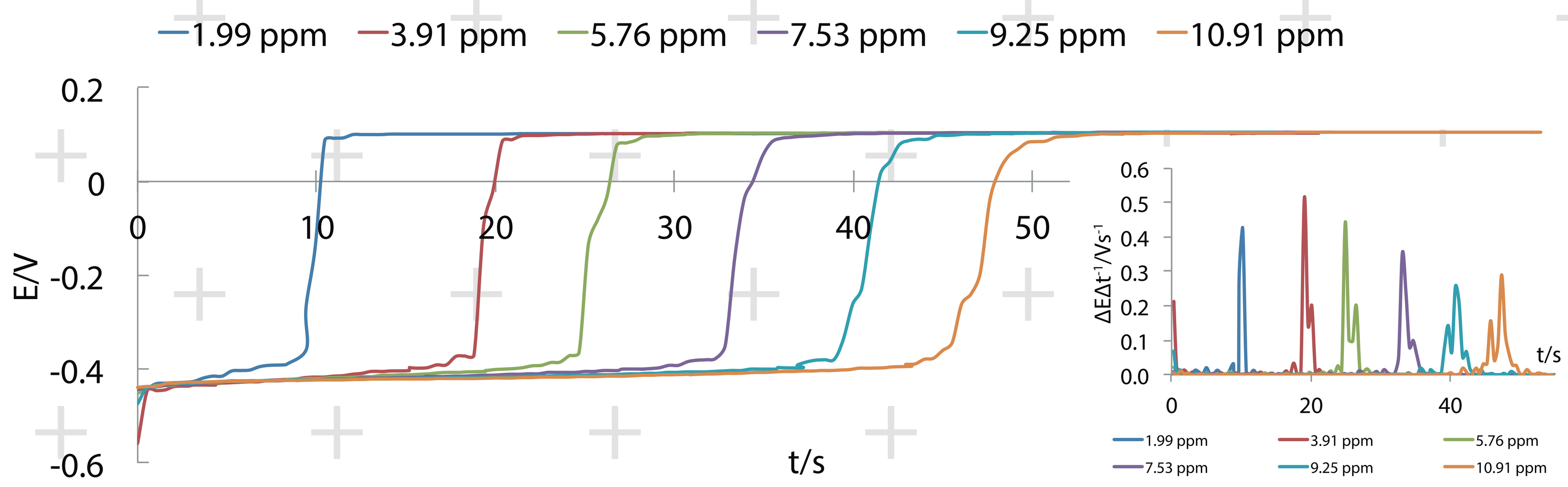

Figure 2. Typical PSA curves. Lead curves are shown. (First derivative analysis is shown at the lower right corner)

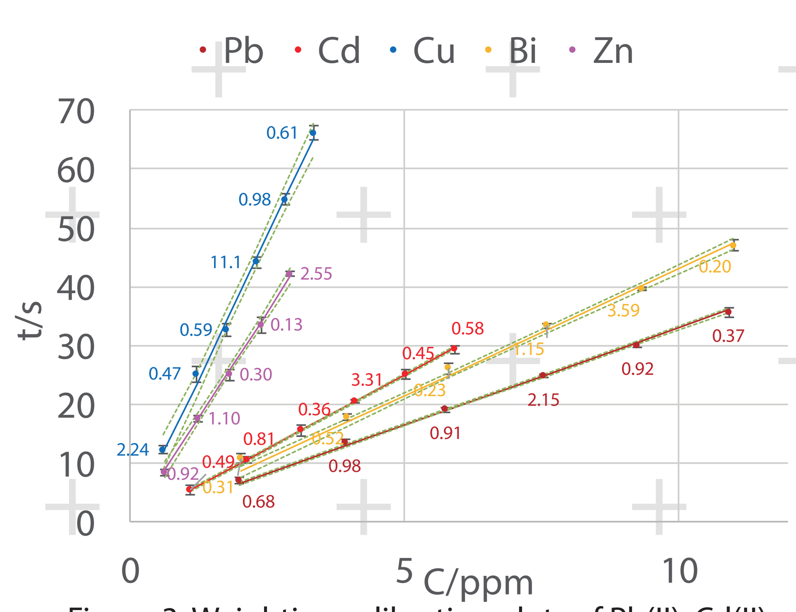

Figure 3. Weighting calibration plots of Pb(II), Cd(II), Cu(II), Bi(II) and Zn(II) at 95% of confidence. Weights are shown for each point

Cation	Lineal equation	LOD ppm	LOQ ppm
Pb(II)	$t=(3.31\pm0.19)s\ ppm^{-1}\ C-(0.03\pm1.34)s$	0.44	1.46
Cd(II)	$t=(5.01\pm0.12)\ s\ ppm^{-1} +(0.00\pm0.46)s$	0.10	0.33
Cu(II)	$t=(19.49\pm1.41)\ s\ ppm^{-1}\ C-(0.03\pm3.14)s$	0.17	0.58
Bi(II)	$t=(4.31\pm0.36)\ s\ ppm^{-1}\ C-(0.04\pm2.66)s$	0.67	2.22
Zn(II)	$t=(14.31\pm1.02)\ s\ ppm^{-1}\ C+(0.04\pm2.00)s$	0.13	0.44

Table 2. Properties of the analytes curves

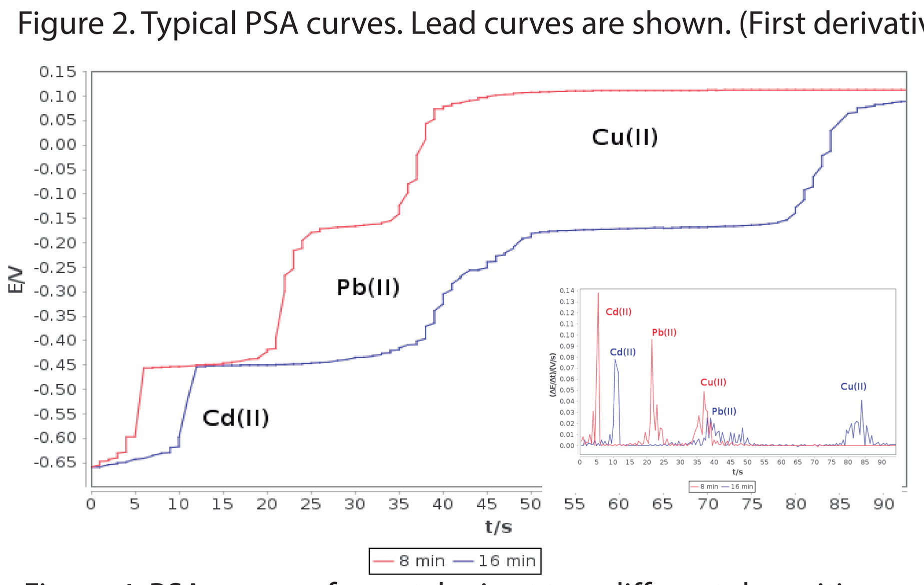

Figure 4. PSA curves of a metal mix at two different deposition times. (First derivative analysis is shown at the lower right corner)

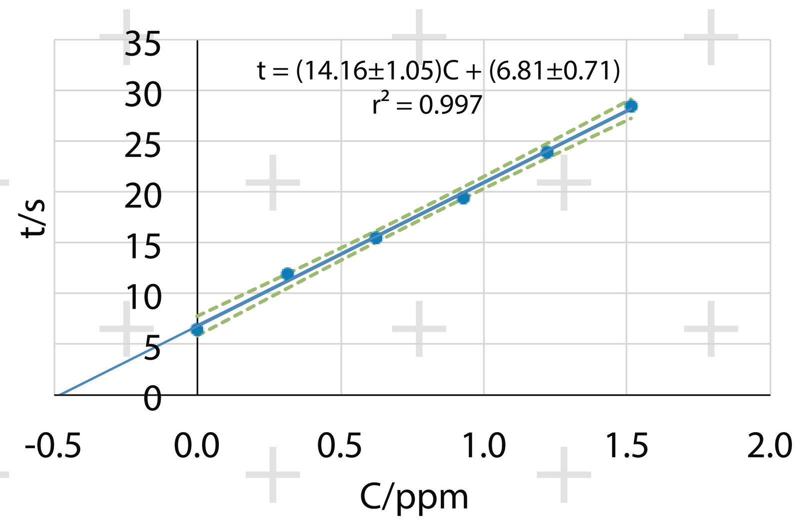

Figure 5. Analysis of an alcoholic beverage at 95% of confidence

Analysis of a mix of metals resulted into the Figure 4. There are as many potential jumps as analytes are present. In addition, doubling the deposition step time resulted in doubling of the transition time.
The analysis of the alcoholic beverage is shown in Figure 5. Due to the transition potential, copper has been identified. According to the results, the content of copper in the alcoholic beverage was (0.48±0.10)ppm.

Conclusions

- A low cost microPSA device has been developed for analysis of low concentrated cations.
- Pb(II), Cd(II), Cu(II), Bi(II) and Zn(II) samples at ppm levels between 10 ppm and 1 ppm can be analyzed by calibration plots.
- A PSA curve of a sample with more than one metal shows as many imposed potential regions as metals are in the sample.

References

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