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BRIEF OVERVIEW OF INSTRUMENTAL METHODS FOR DETERMINATION OF TRACE ELEMENTS IN BIOLOGICAL AND ENVIROMENTAL SAMPLES.
PART II: SEPARATION AND ELECTROANALYTICAL TECHNIQUES

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Summary. Spectroscopic techniques, especially atomic absorption spectrometry, are used most frequently for routine investigation of trace amounts of toxic and physiologically important elements in samples of different origin. However, in some cases, other techniques such as ion chromatography or electroanalytical techniques can be also successfully applied.
In the paper, we present a brief description of both techniques and examples of their application to determine low concentrations of analytes.

Keywords: analytical techniques, ion chromatography, voltammetry, biological samples, ions, elements, trace analysis

INTRODUCTION

Although spectroscopic techniques are used most commonly for trace elemental analysis of various samples, specific analytical problems require other techniques, e.g. ion chromatography is especially useful for speciation analysis, which facilitates determination of different forms of the same element. This is important because individual forms often differ in their toxicity, depending on the degree of oxidation or combination with other components. For example, inorganic arsenite and arsenate are more toxic than organic arsenic species; in contrast, organic mercury forms (methylmercury or ethylmercury) are more dangerous to humans than inorganic ones. Moreover, the simplicity and cost of the procedure is crucial to develop a rapid and low-cost analytical approach; thus, in this case, such techniques as voltammetry should be taken into account. The choice of a proper method depends also on the kind of matrix and analytes, e.g. electroanalytical techniques are more recommended for samples with a high salt concentration (sea water samples).
The aim of this study was to present electroanalytical and separation techniques and examples of their application in trace analysis of samples of different origin.

Ion chromatography

Ion chromatography allows determination of metal and non-metal ions and certain organic compounds, for example, simple sugars. The principle of operation of ion chromatography is the same as in other types of column chromatography - components are retained in the column due to different affinity for the stationary and mobile phase. However, the mechanisms of this affinity are usually different in the case of adsorption chromatography.

The differences in these mechanisms allow distinguishing the following modifications of ion chromatography [1].
- (*High Performance Ion Chromatography* – HPIC);
- (*High Performance Ion Chromatography Exclusion* – HPICE);
- (*Ion Pair Chromatography, Mobile Phase Ion Chromatography* – MPIC);

- (*High Performance Chelation Ion Chromatography* – HPCIC).

Ion chromatography uses columns, where the ionization phase is ionic (cation exchange, anion exchange, or amphoteric ion exchange capable of exchanging both cations and anions). Cationic synthetic resins are most commonly used with immobilized sulfonic groups, while quaternary ammonium bases are used for the determination of anions.

Injected into the chromatography system, the sample is transferred to the column, where ion exchange between ionized and stationary ions occurs. Measured ions move in the column with varying rates, to a large extent depending on the counter-phase type of the mobile phase. The eluent pH and its ionic strength influence ion retention. Selecting the right eluent depends on the type of detector used and the application of elution conductor damping. Examples of the use of ion chromatography in trace analysis are shown in Table 1.

Several types of detectors are used in ion chromatography, and conductometric detectors are of paramount importance. Fluorescent, spectrophotometric, electrochemical, refractometric, radiometric, or atomic absorption detectors are sometimes used as well [2, 3].

The undisputed advantages of ion chromatography include [4, 2, 3]:

- the ability to simultaneously identify multiple types of ions during a single analysis, including the simultaneous determination of organic and inorganic ions;
- possibility of conducting speciation analysis;
- low toxicity of eluents;
- the ability to analyze small quantities of samples;
- low detection limits and quantification (ng / mL);
- the ability to determine ions in a sample within a wide range of concentrations (about 1 ppb - 10 ppm).

Electroanalytical techniques

Some of electroanalytical techniques include potentiometry, coulometry, conductometry, and voltammetry; however, the last one has the greatest significance in contemporary trace analysis.

Voltammetry is an analytical technique in which the measurement of the current flowing through the electrode is used as a function of the applied potential. Three types of electrodes are used in voltammetry: working, reference, and auxiliary. The working electrode is made of a noble metal such as gold, platinum, mercury, or vitreous coal [5]. If this electrode is stationary, the technique is referred to as voltammetry, but if a mercury electrode is used, the technique is polarography.

The reference electrode is an electrode in which the potential of the working electrode is measured. A saturated calomel electrode and a silver chloride electrode are the most commonly used reference electrodes. The auxiliary electrode is usually made of platinum and is intended to provide constant value for the potential of the reference electrode. During the analysis of the sample, the current in the function of the potential is recorded as a voltammogram.

The peak position on a voltammogram or polarogram (in the case of polarography) provides qualitative information, while the peak current allows quantitative analysis.

Three techniques are distinguished within voltammetry method:

- Voltammetry with a linearly changing potential - Linear Sweep Voltammetry - LSV;
- Cyclic Linear Sweep Voltammetry (CLSV);
- Inverted (stripping) voltammetry - Anodic Stripping Voltammetry – ASV, Cathodic Stripping Voltammetry - CSV;
- Voltammetry adsorption - Adsorptive Stripping Voltammetry - AdSV.

Inverted voltammetry is currently the most commonly used technique for determination of metal ions [6, 7]. Its great advantage is high sensitivity (limit of determination up to 10-12 mol / L). Examples of voltammetry applications in trace analysis are shown in Table 2.

CONCLUSIONS

This technique also allows determination of the content of several metal ions present in the sample side by side.

The principle of inverse voltammetry consists in the reduction of metal ions on the working electrode (unregistered process) where the concentration of metal is determined, and then, with the controlled potential of the electrode, its oxidation (anodic dissolution is the process of diffusion) in the form of a voltamperometric wave forms the basis of analytical determination [8-12].

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Table 1. Examples of ion chromatography applications in trace element analysis.

Sample type	**Determined ion**	**Type of column and eluent**	**Type of detector**	**Ref.**
Rainwater	CrO_4^{2-}	Ion Pac CS5A. eluent: 10 mM/L PDCA + 148 mM/L NH_4OH	Spectrophotometric. UV λ=365 nm	[13]
Multifloral honey (Punjab, India)	Ni^{2+}	Ion Pac CG5A+ CS5A. eluent:28 mM/L $(COOH)_2$ +45 mM/L NaCl +116 mM/L $NaNO_3$+40 mM/L HCl	Spectrophotometric. UV. λ=530 nm. with post-column derivatization	[14]
Aqueous soil extract	AsO_4^{3-}	Ion Pac AS11. eluent: 100mM/L NaOH	Mass spectrometry	[15]
Milk- certificated reference material	Cu^{2+}	Ion Pac CG5A+ CS5A. eluent: 28 mM/L $(COOH)_2$ +45 mM/L NaCl+116 mM/L $NaNO_3$+40 mM/L HCl	Spectrophotometric. VIS. λ=530 nm. with post-column derivatization	[16]
Soil	Mn^{2+}	CS5A. eluent: 100 mM/L oxalic acid	Spectrophotometric. VIS. λ=530 nm. with post-column derivatization	[17]
Water, Bahteem lake	Cu^{2+}	HIPIC-CS5A. eluent: 8 mM/L PDCA+ 66 mM/L KOH. 74 mM/L fromic acid	Spectrophotometric. VIS. λ=530 nm. with post-column derivatization	[18]
Well water. Mexico	Zn^{2+}	HIPIC – CS2. eluent: 10 mM/L oxalic acid +7.5 mM/L citric acid	Spectrophotometric. VIS. λ=520 nm. with post-column derivatization	[19]

Table 2. Examples of voltammetry applications in trace analysis.

Sample type	**Element**	**Technique**	**Ref**
Bottled white wine	Pb	Anodic stripping voltammetry	[20]
Mineralizate	Cd	Anodic cyclic stripping voltammetry	[21
River water	Pb	Anodic stripping voltammetry	[22]
Sample of sewage from Changchun province	Pb	Cyclic voltammetry	[23]
Milk	Cd	Anodic stripping voltammetry	[24]
Tap water	Cu	Anodic stripping voltammetry	[25]
Honey from bees without sting, from Guaraquecaba province	Cu	Anodic cyclic stripping voltammetry	[26]
Water from Chinese lake (China)	Cu	Anodic cyclic stripping voltammetry	[27]