Application of catalytic adsorptive stripping voltammetry in water analysis

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Abstract. The application of catalytic adsorptive stripping voltammetry (CAdSV) for the determination of the trace elements in water is presented. The CAdSV, coupling of very efficient adsorptive accumulation of the electroactive species on the electrode surface with the catalytic reaction, provides a significant amplification of the analytical response, and consequently a considerable decrease of the detection limit, as well as an improvement of the selectivity of the determination. The course of the catalytic reactions occurring in catalytic systems, which is most frequently applied in CAdSV analysis, is given. The features and advantages of the CAdSV method and its exploitation in ultratrace analysis of water samples are discussed. Numerous examples of the CAdSV systems, which have found application in the determination of Co, Cr, U, Fe, Mo, Pt, Rh, Ti, W and V, as well as of some anions and organic substances in various kinds of water, are listed.

Keywords. Adsorptive stripping voltammetry; catalytic systems; trace elements water analysis

Introduction

Determination of the traces of elements in natural waters such as river, lake, sea, coastal and ground water samples as well as in wastes requires the application of very sensitive and selective analytical methods. Modern analysis of such media consists not only in the determination of the total concentration of the ultratrace elements varying in the range from 1 ppt to 10 ppb but also in the speciation study of their physicochemical forms (speciation analysis). Voltammetric methods, comprising the selected voltammetric and polarographic techniques, are the most sensitive and selective analytical tools in the determination of both the total concentration of the traces of elements or compounds and their forms such as oxidation step, stability of metal complexes, ionic or non-ionic character, etc.

Voltammetric methods of high sensitivity

High sensitivity of the voltammetric determination of the traces of elements can be achieved in the following ways (Zarebski, 1991):

1. by applying modern voltammetric and polarographic techniques such as Osteryoung square wave voltammetry (OSWV) or differential pulse voltammetry (DPV),
2. by using of new type or design of indicating electrodes such as mercury electrodes, thin mercury film electrodes with metal, graphite or glassy carbon supports, modified electrodes etc.,
3. by utilising the stripping procedures (SV) based on the preliminary electrochemical or adsorptive preconcentration of electroactive species on the surface of the indicative electrode during the accumulation step, and voltammetric determination of the accumulated depolariser by recording the voltammetric curves during the stripping step using linear scan, differential pulse or square wave voltammetric mode,
4. by exploitation of catalytic systems in which the analysed species induce cyclic catalytic reactions on the surface of indicative electrode leading to very high values of analytical response, i.e. faradic current.
The above mentioned methods of increasing the sensitivity of determination are usually combined, for instance, the stripping voltammetric curves are frequently developed by means of the most sensitive voltammetric modes, such as DPV or OSWV.

The extremely high sensitivity of the determination of the traces of elements can be achieved by applying catalytic adsorptive stripping voltammetry (CAdSV) which couples the very efficient adsorptive accumulation of the determined elements in form of complexes with numerous organic and inorganic ligands with the catalytic reaction occurring during the stripping step. The final analytical signal, i.e., faradic current, is therefore the product of the dual amplification effect of interfacial accumulation and catalytic reaction:

\[ i_f = [\text{adsorptive enrichment}] \times [\text{catalytic enhancement}] \]

The methods of adsorptive enrichment have been described in some reviews and papers (Wang, 1985, 1988, Kalvoda and Koganic, 1989, 1994, van den Berg, 1989, 1991, Paneli and Voulgaropoulos, 1993, Prokhorova et al., 1998, Sawamoto, 1999). Among various kinds of catalytic systems (Bobrowski and Zarebski, 2000) the most frequently applied in water analysis are the systems in which the following catalytic reactions occur:

- **Catalytic systems of the first kind**
  \[ \text{Me}^{n+} + \text{me} \Leftrightarrow \text{Me}^{n-m} \]
  \[ \text{Me}^{n-m} + \text{Ox} + (\text{H}^+, \text{H}_2\text{O}) \Rightarrow \text{Me}^{n+} + \text{Red} + (\text{H}_2\text{O}, \text{OH}^-) \]
  where: Me\(^{n+}\) and Me\(^{n-m}\) – oxidized and reduced forms of the depolariser, Ox – an oxidizing agent, Red – the product of catalytic reduction of the oxidizing agent.

  As is seen from eqs. (1) and (2) the depolariser Me\(^{n+}\) can take part many times in the cycles described by eqs. (1) and (2), which leads to a large increase of the faradic current and, therefore, the sensitivity of the determination of the given metal ion Me\(^{n+}\).

- **Catalytic system of the second kind**
  \[ \text{Me}^{n+} + \text{me} \Leftrightarrow \text{Me}^{n-m} \]
  \[ \text{Me}^{n-m} + \text{Ox} \Leftrightarrow \text{Me}^{n-m}\text{Ox} \]
  \[ \text{Me}^{n-m}\text{Ox} + \text{pe} + (\text{H}^+, \text{H}_2\text{O}) \Rightarrow \text{Me}^{n-m} + \text{Red} + (\text{H}_2\text{O}, \text{OH}^-) \]

  As it results from the presented scheme of catalytic reaction the ion-catalyser causes the electrochemical reduction of the voltammetrically inactive ligand (Ox) which also leads to a high increase of faradic current.

- **Composite catalytic systems**

  In these catalytic systems both mentioned catalytic reactions occur stepwise. In the first step catalytic reaction of the first kind produces a ligand which takes part in the catalytic system of the second kind. The example of this type of catalytic system is the well known system Cr(III) with diethylenetriamine-N\(_2\),N,N',N'',N''-pentaacetic acid (DTPA) complexone in the presence of nitrate ions, i.e. Cr(III)•DTPA + NO\(_3\)\(^-\) (Zarebski 1977, 1985).

- **Catalytic systems of hydrogen ions**

  Catalytic systems consisting of a catalyst and hydrogen ions are based on the phenomenon of the overvoltage of the reduction of hydrogen ions at the surface of the indicating electrode. The scheme of catalytic reaction can be written in the following way:
\[
\begin{align*}
\text{Cat} + \text{H}^+ & \rightarrow \text{Cat} \cdot \text{H}^+ \\
\text{Cat} \cdot \text{H}^+ + e & \rightarrow \text{Cat} \cdot \text{H}^0 \\
2 \text{Cat} \cdot \text{H}^0 & \rightarrow \text{Cat} + \text{H}_2
\end{align*}
\]

(6) (7) (8)

where: Cat is the catalyzer, such as noble metal ions, transition metal ions complexes, organic substances etc.

The above mentioned catalyzers give a very high catalytic response with hydrogen ions and the catalytic currents are in most cases proportional to the concentration of the given catalyzer. Considering the fact that the substances catalyzing the reduction of hydrogen ions can be additionally accumulated at the surface of the mercury electrode due to stripping procedures, the catalytic systems of hydrogen belong to the most sensitive voltammetric methods applied in the ultratrace analysis.

Potentialities of CADSV method

The CADSV also enables us to increase the selectivity of determination. Better selectivity results from enhancing the ratio of the analytical response of an ion-catalyzer to the analytical response of other species and from the specificity of catalytic reaction of a given ion-catalyzer with the given catalytic agent. The application of catalytic systems of different kind discussed in detail elsewhere (Bobrowski and Zarebski, 2000), also extends the range of concentration of the species inducing these reactions. In certain cases catalytic systems also offer the possibility of the determination of electrochemically inactive ions or compounds taking part in the reactions.

CADSV enables the determination of these elements, whose ions after reduction do not form amalgams, but form metal films at the surface of the electrode. Some speciation studies can also be performed by means of CADSV (see Table 1, Scholz et al., 1990, Mrzljak et al., 1993, Gao and Siow, 1996a,b, Aldrich and van den Berg, 1998, Korolczuk and Grabarczyk, 1999a, 1999b).

Application of the CADSV in routine analysis of water

The numerous examples of the CADSV procedures, which have found application in the determination of Co, Cr, U, Fe, Mo, Pt, Rh, Ti, W, V and some anions in various kinds of water, are presented in Table 1.

Some analytical CADSV procedures were found to be especially useful for in-situ continuous monitoring of trace metals amounts (Mrzljak et al., 1993, Achterberg and van den Berg, 1994, Colombo et al., 1997) and speciation study (Achterberg and van den Berg, 1994) in natural waters. For this purpose some automatic voltammetric analyzers enabling semi-continuous monitoring have been designed. The elaborated automatic analyzers have been applied for continuous flow or flow injection analysis.

CADSV allows us to determine the low concentrations, however, full utilization of this method is possible by providing appropriate conditions. The determination of ultratrace amounts of elements by the CADSV method is often hampered by the dissolved organic matters (DOM) present in the analyzed solutions. These substances may form complexes with the determined metal ions or may show the surface-active properties (SAS). In both cases we can observe the interference caused either by blocking the electrode surface or by forming various complexes reduced at different potential. As a result, the presence of DOM in the solution may reduce the sensitivity of the determination or even completely eliminate the voltammetric signal. For this reason the voltammetric analysis must be preceded by the decomposition of DOM by UV irradiation or by microwave mineralization. Some automatic voltammetric analyzers containing in-line UV-digestion unit (Achterberg and van den Berg, 1994, Colombo et al., 1997) make the continuous removing
### Table 1 Application of CadSV in Water Analysis

<table>
<thead>
<tr>
<th>Metal</th>
<th>Sample Matrix</th>
<th>Complexing agent</th>
<th>Catalytic agent</th>
<th>Remarks</th>
<th>Refs.</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>Seawater</td>
<td>Nioxime</td>
<td>NO$_2^-$</td>
<td></td>
<td>Vega et al., 1997</td>
</tr>
<tr>
<td></td>
<td>Seawater</td>
<td>$\alpha$-benzyl dioxime</td>
<td>NO$_2^-$</td>
<td>On-line at HMDE</td>
<td>Colombo et al., 1997</td>
</tr>
<tr>
<td>Oceaan</td>
<td>Seawater</td>
<td>$\alpha$-benzyl dioxime</td>
<td>NO$_2^-$</td>
<td></td>
<td>Golimowski et al., 1995</td>
</tr>
<tr>
<td>Municipal sewage</td>
<td>Seawater</td>
<td>$\alpha$-benzyl dioxime</td>
<td>NO$_2^-$</td>
<td></td>
<td>Golimowski et al., 1994</td>
</tr>
<tr>
<td>Natural waters</td>
<td>Natural waters</td>
<td>2-aminocyclopentene-1-dithiocarboxylic acid</td>
<td>NO$_2^-$</td>
<td></td>
<td>Ensafii, 1999</td>
</tr>
<tr>
<td>Cr</td>
<td>Natural waters, seawater</td>
<td>DTPA</td>
<td>NO$_3^-$</td>
<td></td>
<td>Golimowski et al., 1985</td>
</tr>
<tr>
<td></td>
<td>Seawater</td>
<td>DTPA</td>
<td>NO$_3^-$</td>
<td>On-line at HMDE</td>
<td>Achterberg et al., 1994</td>
</tr>
<tr>
<td></td>
<td>Water reactor</td>
<td>DTPA</td>
<td>NO$_3^-$</td>
<td></td>
<td>Torrance et al., 1987</td>
</tr>
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<td></td>
<td>Natural waters</td>
<td>TTHA</td>
<td>NO$_3^-$</td>
<td></td>
<td>Paneli et al., 1993</td>
</tr>
<tr>
<td></td>
<td>Sea and tap waters</td>
<td>DTPA</td>
<td>NO$_3^-$</td>
<td>Cr speciation</td>
<td>Scholz et al., 1990</td>
</tr>
<tr>
<td></td>
<td>Brine</td>
<td>DTPA</td>
<td>NO$_3^-$</td>
<td>FIA</td>
<td>Romanus et al., 1991a</td>
</tr>
<tr>
<td></td>
<td>Brine</td>
<td>DTPA</td>
<td>NO$_3^-$</td>
<td>CFA</td>
<td>Budnikov et al., 1994</td>
</tr>
<tr>
<td></td>
<td>Natural waters</td>
<td>DTPA</td>
<td>NO$_3^-$</td>
<td>On-line at MFGCE</td>
<td>Dobney et al., 1994</td>
</tr>
<tr>
<td></td>
<td>Natural waters</td>
<td>Bipyridyl</td>
<td>NO$_2^-$</td>
<td></td>
<td>Gao et al., 1996a</td>
</tr>
<tr>
<td>Ground waters</td>
<td>Natural waters</td>
<td>DTPA</td>
<td>NO$_3^-$</td>
<td>Cr and U</td>
<td>Wang et al., 1997</td>
</tr>
<tr>
<td>Fe</td>
<td>Seawater</td>
<td>1-Nitrozo-2-naphthol</td>
<td>H$_2$O$_2$</td>
<td></td>
<td>Gao et al., 1996b</td>
</tr>
<tr>
<td></td>
<td>Seawater</td>
<td>1-Nitrozo-2-naphthol</td>
<td>BrO$_3^-$</td>
<td>Fe speciation</td>
<td>Aldrich et al., 1998</td>
</tr>
<tr>
<td></td>
<td>Natural waters</td>
<td>CNS</td>
<td>NO$_3^-$</td>
<td></td>
<td>Gao et al., 1996b</td>
</tr>
<tr>
<td></td>
<td>Tap water</td>
<td>5-Br-PADAP</td>
<td>NO$_3^-$</td>
<td></td>
<td>Wan et al., 1999</td>
</tr>
<tr>
<td>Ge</td>
<td>Mineral waters</td>
<td>Gallic acid</td>
<td>V(V)-EDTA</td>
<td></td>
<td>Jiang et al., 1998</td>
</tr>
<tr>
<td>Mo</td>
<td>Natural waters</td>
<td>Mandelic acid</td>
<td>ClO$_3^-$</td>
<td></td>
<td>Pelzer et al., 1989</td>
</tr>
<tr>
<td></td>
<td>Natural waters</td>
<td>8-hydroxyquinoline</td>
<td>NO$_3^-$</td>
<td>CFA at MFGCE</td>
<td>Navratilova et al., 1991</td>
</tr>
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<td>Standard solutions</td>
<td>8-hydroxyquinoline</td>
<td>NO$_3^-$</td>
<td></td>
<td>Neto et al., 1994</td>
</tr>
<tr>
<td></td>
<td>Natural waters</td>
<td>naphthalen-2,3-diol</td>
<td>BrO$_3^-$</td>
<td></td>
<td>Li et al., 1997</td>
</tr>
<tr>
<td></td>
<td>Mineral waters</td>
<td>methylthymol-blue</td>
<td>ClO$_3^-$</td>
<td></td>
<td>Safavi et al., 1999</td>
</tr>
<tr>
<td>Pt</td>
<td>Sea, natural waters</td>
<td>H$^+$</td>
<td></td>
<td></td>
<td>Wang et al., 1987</td>
</tr>
<tr>
<td>Sb + Sn</td>
<td>Dust, river sediments</td>
<td>Ferron</td>
<td>H$^+$</td>
<td></td>
<td>Wei et al., 1994</td>
</tr>
<tr>
<td></td>
<td>Waters, wastes</td>
<td>Ferron</td>
<td></td>
<td></td>
<td>Wei et al., 1996</td>
</tr>
<tr>
<td>V</td>
<td>Seawater</td>
<td>Catechol</td>
<td>BrO$_3^-$</td>
<td></td>
<td>Vega et al., 1994</td>
</tr>
<tr>
<td></td>
<td>Waters</td>
<td>DHN</td>
<td>BrO$_3^-$</td>
<td></td>
<td>Li et al., 1996</td>
</tr>
<tr>
<td></td>
<td>Sea, natural waters</td>
<td>Cufperron</td>
<td>BrO$_3^-$</td>
<td>On-line at MFGCE</td>
<td>Greenway et al., 1995</td>
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<td></td>
<td>Tap water</td>
<td>Quercetin</td>
<td>ClO$_3^-$</td>
<td></td>
<td>Tuo et al., 1996</td>
</tr>
<tr>
<td></td>
<td>River waters</td>
<td>Gallocyanine</td>
<td>BrO$_3^-$</td>
<td></td>
<td>Li Z.J. et al., 1998</td>
</tr>
<tr>
<td></td>
<td>Natural waters</td>
<td>EBR + DPG</td>
<td>BrO$_3^-$</td>
<td></td>
<td>Li Z.J. et al., 1998</td>
</tr>
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<td>NH</td>
<td>Sea water</td>
<td>Formaldehyde</td>
<td>H$^+$</td>
<td></td>
<td>Harbin et al., 1993</td>
</tr>
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<td>Anions</td>
<td>Natural waters</td>
<td>T(III)-C$_4$I$_4^-$</td>
<td>ClO$_4^-$</td>
<td></td>
<td>Neuholt et al., 1996</td>
</tr>
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<td></td>
<td>Natural waters</td>
<td></td>
<td>Me$^{+2}$</td>
<td></td>
<td>Markusova, 1989</td>
</tr>
</tbody>
</table>

**Abbreviations:**

- DTPA – diethylenetriamine-N,N,N',N'',N''-pentaacetic acid,
- TTHA – triethylene-triamine-N,N,N',N'',N''',N'''-hexaaxetic acid,
- Ferron – 7-iodo-8-hydroxyquinoline-5-sulfonic acid,
- DHN – 2,3-dihydroxynaphthalene,
- EBR – eriochrome black R,
- DPG – diphenylguanidine,
- FIA – Flow injection automated system,
- CFA – Continuous flow at a wall-jet,
- HMDE – Hanging mercury drop electrode,
- MFGCE – Modified film glassy carbon electrode,
- MCPE – Modified carbon paste electrode.
of the DOM from the determined samples possible without any additional, separate decomposition step.

In the CAdSV analysis, as in other methods of ultratrace analysis, it is necessary to use high purity reagents and water. Usually, air in a conventional laboratory contains dusts, mists and fumes circulating in the atmosphere and polluting the analyzing water samples in the open vessel. Hence, to eliminate the influence of the laboratory environment on the analytical results it is recommended to perform the experiments in special chambers with laminar flow, i.e. clean laboratories with 100- and 1000-class clean rooms or in smaller 1000-clean flow boxes. The controlled laboratory conditions provide the constant value of the low blank level, lower detection limit and highest precision.

Conclusions
The coupling of the catalytic reaction with the adsorptive stripping voltammetry significantly increases the sensitivity and selectivity of the voltammetric determination. In optimal conditions the method enables us to analyse some trace elements in aqueous media with the determination limit up to 1 ppt. Therefore, CAdSV has found numerous applications in the determination of the traces of some metal ions, anions and organic compounds in various kinds of inland, ground and ocean waters (Table 1). The method is especially recommended for the analysis of water solutions, containing high concentrations of salts (seawater, brine, mine waters etc.). In these cases the CAdSV is more effective than ICP MS or flameless ASA methods. Moreover, the cost of laboratory equipment is lower when compared with the other analytical methods. The CAdSV method is especially useful for in-situ continuous monitoring of trace metal amounts and speciation study in natural waters.

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