BIAMPEROMETRIC DETECTION IN FLOW-INJECTON ANALYSIS.

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ABSTRACT

Amperometric detection with two polarized electrodes, if used with appropriate masking procedures, can be successfully applied in flow-injection determinations in routine analysis. Different applications including direct, indirect, catalytic and single point titrimetric determinations are reviewed.

Introduction

In analytical amperometric techniques the concentration of an electroactive substance is measured by the current which results from its reaction at an electrode. Amperometry with a single polarized indicating electrode in a conjuction with a non-polarizable reference electrode was derived directly from polarography. Most of its applications were developed for end-point detection in titrations [1-3]. The applications of different kinds of amperometric detection in flow analysis were reviewed by Trojanowicz [4].

The idea of using of a change in current between two identical indicating electrodes to detect titration end point was originated already in 1987 by Salomon [5] and further developed as *dead-stop end point method* by Foulk and Bawden [6]. The theory of such a detection method was discussed by Stock [1] and Lingane [3].

The amperometric detection with two polarized indicating electrodes (also named as *biamperometric detection*) is based on the measurement of the intensity of current passing through the two identical, usually inert, electrodes, to which a small potential difference from few tens to few hundreds millivolts was applied. The current flowing in the detection cell is observed only, when solution contacting the electrodes contains two forms of reversible redox couple, it means such one for which at the same potential the oxidation of the reduced form or the reduction of oxidized form can occur. This behaviour is observed for such couples as Br_2/Br^-, Fe(III)/Fe(II), $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$, Ce(IV)/Ce(III), I_2/I^-, Ti(IV)/Ti(III), VO_3^-/VO^{2+} and quinone/hydroquinone [3]. Cu(II)/Cu(I) system was found reversible in nonaqueous media and was utilized for biamperometric titration [8]. The process of the oxidation of a metallic silver and reduction of silver metal ions is also reversible and was used for the determination of silver ions [9].

In biamperometric detection, in the presence of an excess of one form of reversible redox couple, the magnitude of the current measured is linearly proportional to the concentration of the second form in the solution as long as concentration overpotential is not involved. When the polarizing potential difference applied to the electrodes is increased, an extention of the linear range of response is observed, however, it is associated with possible interference for other redox species present in solution. When the system detected in the solution is irreversible, the oxidation and reduction processes have activaion potentials much larger, even up to 1 V. Such a large polarizing potential difference is also applied in biamperometric detection carried out in non-aqueous solvents [7].

Applications of biamperometry in non-flow conditions

As it is demonstrated in the monograph by Songina [2] and several reviews by Stock [10], the most often application of biamperometric detection is the indication of end point in dead-stop titrations and in titrations with electrochemically generated titrant.

Lingane [3] has pointed out, that sensitivity of biamperometric detection depends mostly on electrochemical properties of a given reversible couple. An

increase of area of the indicating electrodes leads to the increase of current, however, it is associated with increase of background current, which unfavourable deteriorates the S/N ratio. Usually for that purpose plate or wire indicating electrodes of few to few tens square millimeters are used, most often made of platinum [11-15]. Some authors have reported the use of graphite electrodes [16]. Recently in biamperometric determination of nitrosoamine lower residual currents were observed for gold than for platinum electrode [17].

In the indirect biamperometric detection the analyte reacts selectively with one form of the indicating redox couple. Most frequently iodine/iodide system is used as indicating one in biamperometric titrations [11-14], although other systems were also reported [7,18].

The first application of biamperometric detection in flow analysis with two open-tubular carbon electrodes was reported by Attiyat and Christian [19[for the determination of ethanol, lactate and glycerol using immobilied enzymes with detection of hexacyanoferrate(II) ion produced.

Applications in flow-injection analysis

The first application of direct biamperometric detection in flow-injection analysis (FIA) was reported by Tougas *et al.* [20] for the determination of iron(II) by the injection of sample soution into acidic solution of iron(III). The flow cell with two platinum electrodes (Fig.1) was used. For model studies with $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ system it was found that the linearity of response can be

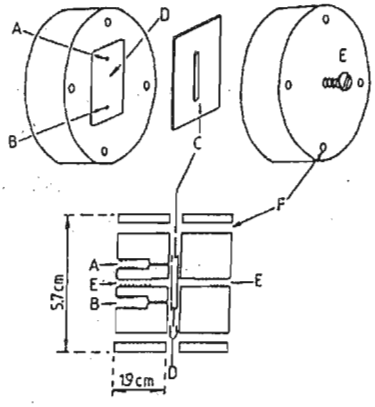

Fig.1. Three-dimensional and cross sectional representation of the biamperometric detector cell: (A) inlet; (B) outlet; (C) Teflon spacer; (D) platinum electrodes; (E) electrode contacts; (F) holes for machine bolts [20].

expanded by the increase of polarizing voltage. For the direct determination of iron (II), a high selectivity of determination in the presence of ascorbic acid was found.

As it is shown in Table 1 the majority of flow injection determinations with biamperometric detection is based on indirect measurements with I_2/I^- indicating system. Determination of nitrite is based on iodide oxidation by analyte,

Table 1. Applications of biamperometric detection in flow-injection analysis.

Determined species	Real matrix	Procedure (indicating system)	Polarazing voltage, mV	Limit of detection, µg/l	Ref.
Fe(II)	Multivitamin preparations	Direct	50-150	N.E. a)	20
Cu(II)	Blood plasma	Indirect (Fe(III)/(II))	80	N.E.	25
Mo(VI)	Soil extracts	Indirect, catalytic (I_2/I^-)	100	1.2	26
NO_2^-, NO_3^-	Waters	Indirect (I_2/I^-)	100 100	6 (for both analytes) 40 (NO_2^-),70 (NO_3^-)	21 22
Acids	-	Indirect, titration (I_2/I^-)	100	N.E.	31
Chlorine, Cu(II)	Swimming pool water	Indirect (I_2/I^-)	100	2 (Cl_2) 60 (Cu(II))	23
Promazine, thioridazine	Tablets	Indirect (Fe(III)/(II))	150	400 500	28
Water	-	Indirect (I_2/I^-)	100	N.E.	29
Reducing sugars, sucrose	Syrups	Indirect $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$	200	N.E.	27
S(II) compounds	-	Indirect b) (I_2/I^-)	25	0.1 - 0.2	30

a) N.E. - not estimated
b) with application of the induced iodine/azide reaction

whereas for determination of nitrate on-line reduction of analyte in microcolumn containing copperized cadmium is used [21,22]. In the flow-through detector two platinum wire electrodes were used (Fig.2), which exhibited a larger sensitivity

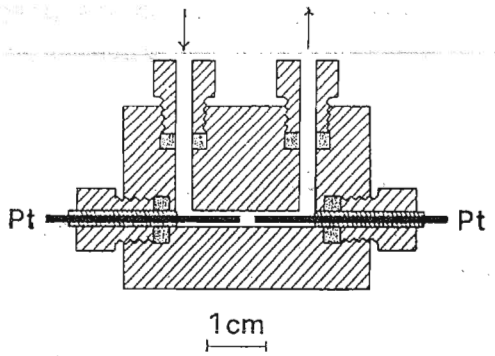

Fig.2. Schematic diagram of the flow cell with two platinum wire electrodes [21-28,31].

of response then the flow cell with semitubular electrodes made of teflonized graphite. The optimization of measuring conditions in single component determinations [21] was utilized later for simultaneous determinations of nitrite and nitrate in natural waters [22]. Sample containing nitrite and nitrate was split into

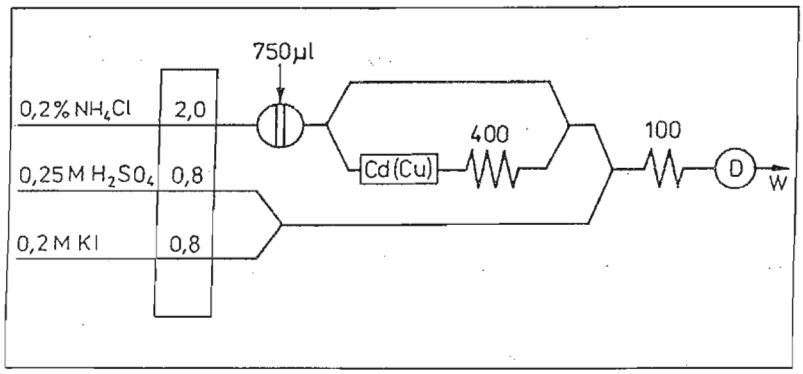

Fig.3. Schematic diagram of manifold used for simultaneous flow-injection biamperometry of nitrite and nitrate [22].

two branches of manifold (Fig.3) , one with reducing column and delay coil and other without those devices, and then two sample segments were again merged in the same stream transported to the detector. For each sample injection two peaks were obtained corresponding to the content of nitrite and sum of nitrite

and nitrate The interference caused by the presence of iron (III) and copper (II) was eliminated by masking, whereas chromium(VI) interference was reduced using anionite Dowex-1 [22].

Using the same indicating system and the same detector design biamperometric methods of flow-injection determination of residual chlorine in waters and simultaneous determination of residual chlorine and copper(II) were developed [23]. This principle was later utilized also for the development of method of continuous monitoring of gase-phase chlorine, based on trapping of chlorine through the walls of a microporous polypropylene tube into an appropriate flowing recipient buffer [24]. In the FIA system for the simultaneous determination of residual chlorine and copper(II) (Fig.4A) a special design of an

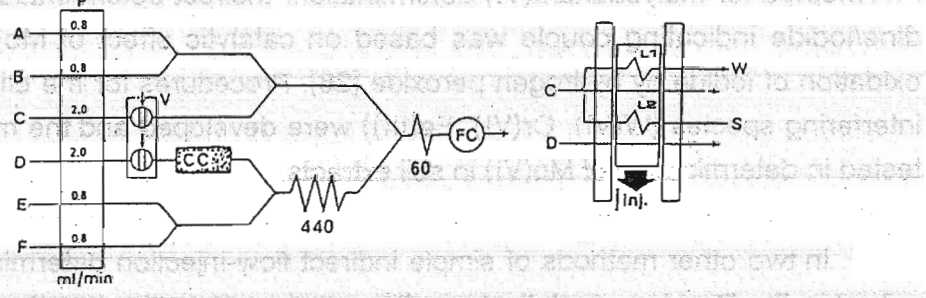

Fig.4. Schematic diagram of the manifold and injection valve used for the simultaneous determination of residual chlorine and copper(II). Solutions: A, 0.2 M KI + 0.5 g l^{-1} EDTA; B, 0.1 acetate buffer pH 4.0; C, distilled water, D, 5 mM acetate buffer pH 4.0; E, 0.2 M KI; F, 0.1 M acetate buffer pH 4.0+10 mM NaF. Components: P, peristaltic pump; CC, charcoal microcolumn; V, injection valve; S, sample injection; W, waste; L1,L2, sample loops [23].

injection valve (Fig.4B) was employed, enabling simultaneous injection of two portions of the same sample solution into two different carrier streams. In one branch of the system for detection of copper a charcoal column was incorporated in order to remove chlorine and also a delay coil. In the second branch of the system for detection of chlorine, the copper(II) present in the sample solution was masked using EDTA. After each injection two peaks were recorded of heights corresponding to the content of both analytes. In a single component

system the detection limit for residual chlorine was 2 μg/l at a sampling rate 120 h^{-1}, however, in two analyte system the detection limit was poorer (20 μg/l) because of the much larger dispersion.

Another FIA method developed for the determination of copper in blood plasma was based on the catalytic effect of Cu(II) on the oxidation of thiosulphate by Fe(III) [25]. The amount of Fe(II) produced in this reaction was proportional to the Cu(II) concentration present in blood plasma. In determinations with a sampling rate of 70 h^{-1} a satisfactory agreement was obtained between FIA biamperometry and flame atomic absorption spectrometry and routinely used precipitation of proteins was the only sample pretreatment required for this complex matrix.

The catalytic effect of analyte was also exploited in the development of FIA method for molybdenum(VI) determination. Indirect determination using iodine/iodide indicating couple was based on catalytic effect of Mo)VI) on the oxidation of iodide by hydrogen peroxide [26]. Procedures for the elimination of interfering species (W(VI), Cr(VI), Fe(III)) were developed and the method was tested in determination of Mo(VI) in soil extracts.

In two other methods of simple indirect flow-injection determination described in the literature analytical results were based on the reaction of analyte with oxidized form of indicating reversible redox couple. The simultaneous determination of sucrose and reducing sugars was based on reduction of hexacyanoferrate(III) by simple carbohydrates in a strongly alkaline medium at elevated temperature [27]. In simultaneous determination of glucose and sucrose the latter was on-line hydrolyzed in hydrochloric acid in the system with two injection valves shown in Fig.5.The sample solution injected with valve V_1 reacts with hexacyanoferrate(III) and after cooling in a 100 cm delay coil and debubbling is transported to the detector. When injected with valve V_2, first the sample compounds are hydrolyzed, and then react with hexacyanoferrate(III). Sucrose and glucose were determined with a sampling rate of 40 h^{-1} in natural samples from a sugar production process.

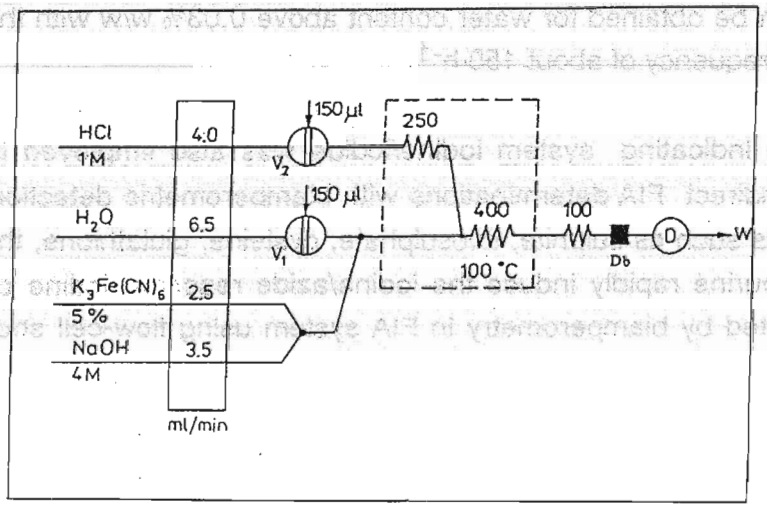

Fig.5. Schematic diagram of the optimized flow-injection system used for the simultaneous determination of sucrose and reducing sugars with biamperometric detection. D, flow-through amperometric detector; DB, debubbler; V_1,V_2, injection valves [27].

The determination of phenothiazine derivatives, which are widely used as antipsychotic pharmaceuticals with biamperometric detection is also based on chemical oxidation of analyte by the oxidized form of indicating redox couple. Among seven different indicating systems examined the most suitable one for the determination of promazine and thioridazine was found to be the redox system Fe(III)/Fe(II) [28]. The method developed was successfully applied to several commercial pharmaceutic preparations.

Biamperometric detection is often employed as detection method in conventional determination of water content in nonaqueous solvents with Karl Fischer method. A flow-injection version of such a determination was also reported with the use of thin-layer detector with two Pt plate electrodes [29]. A design of the flow-cell was similar to that reported by Tougas *et al.* [20]. In the developed method with a two-component pyridine-free K.Fischer reagent the detection is based on the use of iodine/iodide indicating system. In the determination of water in methanol, ethanol and 2-propanol it was found, that satisfactory

results can be obtained for water content above 0.03% w/w with the maximum sampling frequency of about 150 h^{-1}.

The indicating system iodine/iodide was also employed in two more complex indirect FIA determinations with biamperometric detection. Sulpur(II) compounds such as sulphite, thiosulphate, cysteine, glutathione, thiourea or 6-mercaptopurine rapidly induce the iodine/azide reaction. Iodine consumption was detected by biamperometry in FIA system using flow-cell shown in Fig.6 [30].

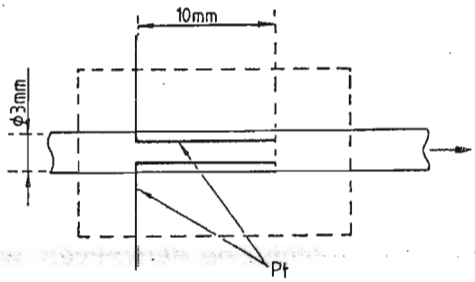

Fig.6. Schematic diagram of the flow cell with two platinum wire electrodes [30].

Indirect biamperometric detection based on reaction:

$$IO_3^- + 8\,I^- + 6\,H^+ = 3\,I_3^- + 3\,H_2O$$

was also utilized for flow-injection single-point titration of acids [31]. The slope of the calibration plots in the milimolar range depends on the strength of the acid. The method was tested for sulphuric, hydrofluoric, monochloroacetic, formic and acetic acids.

Conclusions

The amperometry with two polarized electrodes is simple and rapid method of electrochemical detection although with very limited selectivity. As it is proved by published papers, especially for indirect biamperometric detection, numerous developed FIA procedures can find significant practical application in routine analysis. In the majority if indicated applications it is indispensable to consider carefully all possible interferences from other components of matrices and the use of appropriate procedure of their elimination. In numerous cases the use of flow-injection biamperometry allows to replace more complex spectrophotometric, chromatographic or titrimetric methods.

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