SCIENTIFIC PAPERS
OF THE UNIVERSITY OF PARDUBICE
Series A
Faculty of Chemical Technology
3 (1997)

STUDY OF CONDITIONS FOR VOLTAMMETRIC DETERMINATIONS OF IODINE AT CARBON PASTE ELECTRODES

Jiří KONVALINA[a], Ivan ŠVANCARA[a], Karel VYTŘAS[a1]
and Kurt KALCHER[b]
[a]Department of Analytical Chemistry, University of Pardubice,
CZ-532 10 Pardubice
[b]Institute of Analytical Chemistry, Karl-Franzens University,
A-8010 Graz

Received September 12, 1997

A method has been developed for the determination of iodine in the form of iodide at a carbon paste electrode (CPE) with tricresyl phosphate as a pasting liquid using differential pulse cathodic stripping voltammetry. The determination is based on the combined preconcentration mechanism of iodide anions from acidic media, probably forming ion-pairs with protonated molecules of a pasting liquid, then oxidizing to iodine at +0.7 V (vs. Ag/AgCl) and extracting onto a CPE. The detection limit of 30 $\mu g\ l^{-1}$ was obtained. The procedure was successfully applied to analyse real samples of mineral water and table salts containing either iodide or iodate. The results were verified by means of reference methods, e.g. ICP-MS technique, recovery determinations and iodometric titrations.

---

[1] To whom correspondence should be addressed.

Introduction

The voltammetric determination of iodine in different samples, which could contain various species such as iodide, iodate and also iodine itself, is commonly performed using a stripping technique with hanging mercury drop electrode [1,2], that exploits the formation of an insoluble compound at the electrode surface. Using a silver electrode [3], analogous principles of accumulation followed by cathodic stripping are applicable. The conversion of iodine to iodoform [4] can also be applied; in this case, stationary mercury electrode in nonaqueous medium is used. All the above procedures can serve as examples of stripping voltammetry with traditional types of electrodes.

During recent years, carbon paste electrodes (CPEs) became attractive in electroanalytical chemistry, especially in voltammetry and potentiometry [5,6]. In stripping voltammetry, the advantage of using CPEs is the possibility to preconcentrate the analytes in several different ways, such as electrolysis, adsorption, extraction, ion-pairing or amalgamation in a mercury film previously deposited at the surface of a CPE.

The main aim, in this case, was the determination of iodine using stripping voltammetry with a CPE. Up to this time, only two articles have been published where the voltammetric determination of iodide using a CPE is described. In both cases, the carbon pastes were modified with a suitable chemical compound that gave them some ion-pairing capability [7] or the possibility to anion-exchange [8], on the other hand.

Experimental investigations of the most important parameters of iodide determination, i.e., the choice of the most suitable pasting liquid, conditions for both accumulation and stripping procedures etc., are given in this paper.

Experimental

Apparatus

Measurements were mostly carried out using a PA-3 polarographic analyser (Laboratorní přístroje, Praha), some analytical parameters were evaluated also using a PAR 174A device (Princeton Applied Research). A three-electrode cell was used for measurements, consisting of a CPE as the working electrode, silver-silver chloride and a platinum wire as reference and counter electrodes, resp.

Preparation of CPEs

The carbon pastes were prepared by mixing the graphite powder (0.5 g) and the selected pasting liquid (0.2 ml) as described elsewhere [9]. Uvasol (Uv), silicone oil (SO) and tricresyl phosphate (TCP) were tested as pasting liquids. For each scan, the CPE surface was removed using a wet filter paper.

Preparation of Samples

A sample of a table salt (about 3 g) was weighed, dissolved in redistilled water and adjusted by several drops of conc. hydrochloric acid to pH 1 before filling up to 100 ml. If the table salt contained iodate instead of iodide, hydrazine hydrochloride (ca. 0.5 g) was added. The treatment of the mineral water sample

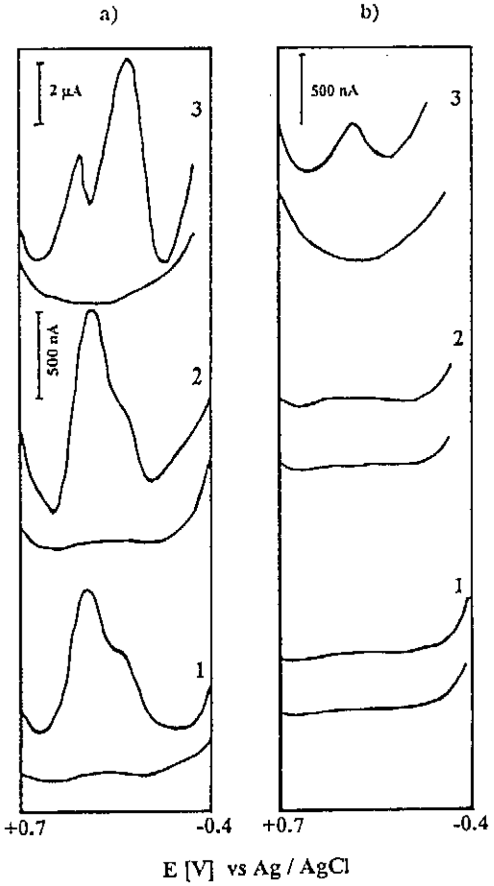

Fig. 1 Comparison of recorded voltammograms for CPEs with different pasting liquids:

a) base line and addition of 50 μl 0.01 M KI for (1) CPE/Uv; (2) CPE/SO and (3) CPE/TCP

b) base line and addition of 200 μl 1×10^{-4} M KI for (1) CPE/Uv; (2) CPE/SO and (3) CPE/TCP

Experimental conditions: PA-3, deposition time - 5 min, supporting electrolyte - 0.1 M HCl (V = 20 ml) consisted in removing CO_2 *via* sonication and adjusting the pH 1 value again with HCl.

Results and Discussion

Influence of Pasting Liquid on Determination of Iodine

The extraction capabilities of CPEs are predominantly governed by character of pasting liquid [9]. Three of them (Uv, SO, TCP) were investigated [10]; based on these experiments, tricresyl phosphate was found the best. It should be noted that this compound was also favoured in CPEs for the determination of gold, which can serve as a suitable example of stripping voltammetry with extractive accumulation [11,12].

The influence of a pasting liquid is shown in Fig. 1, where voltammo-

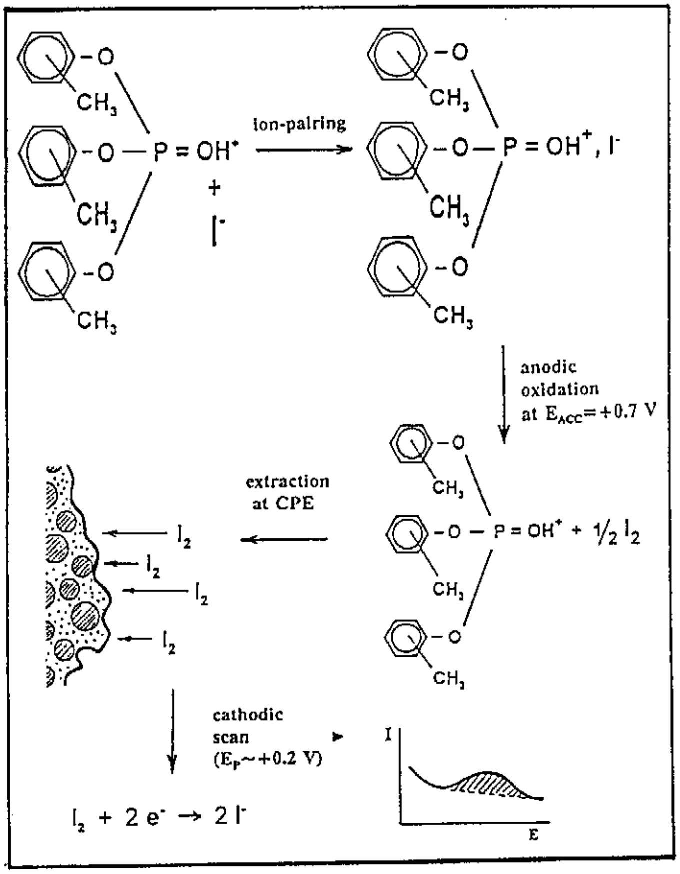

Fig. 2 Possible scheme of accumulation and whole voltammetric procedure of the iodine determination at CPE/TCP

grams taken with three different CPEs are compared. The responses for CPE/Uv (1) and CPE/SO (2) for higher additions of iodide (Fig. 1a) are almost similar, confirming probably analogous accumulation principles. The increased response at the CPE/TCP can be explained on the basis of ion-pairing between protonated molecules of TCP and iodide (the other two liquids have no protonation ability or very low one). For lower concentration of iodide under similar experimental conditions, the measurable response was obtained only at the CPE/TCP (Fig. 1b).

Accumulation Mechanism

In principle bringing enough analyte to the surface of a working electrode is the most important point when using stripping voltammetric techniques [13]. A probable mechanism of accumulation of iodide from acidified solution of the sample (pH 1) is shown in Fig. 2. It is expected that, in the first step, the protonated molecules of TCP form ion-pairs with iodide at the CPE surface. This is followed by anodic oxidation of iodide to iodine at an accumulation potential of +0.7 V vs. Ag/AgCl and its immediate extraction onto a CPE pasting liquid. It was found necessary to keep the analyte in the form of iodide, because no satisfactory response for other species could be recorded. Samples of table salt containing iodate had to be reduced first with a suitable chemical reagent, e.g. hydrazine. When the preconcentration was completed, the reduction of accumulated iodine followed by introducing a cathodic scan and characteristic wide peaks were recorded. It should be mentioned that, in fact, both the accumulation and stripping reactions may be influenced by numerous side equilibria, such as triiodide formation, protonation of iodide and triiodide, etc. This fact perhaps could also explain the wide shape of the peak. The real voltammograms for table salt samples are shown in Fig. 3. An evident difference in shape of both peaks could perhaps be explained as an influence of added hydrazine, but this was not verified.

Calibration

The experimental measurements were performed in a model electrolyte of acidified NaCl (exactly, the mixture of 0.5 M NaCl and 0.1 M HCl) with standard additions of KI (from 5×10^{-7} to 5×10^{-6} mol l^{-1}); the observed voltammograms are shown in Fig. 4. The curves were evaluated first as a dependence of a peak height vs. concentration of iodide (Fig. 5) and secondly as a dependence of a peak area vs. iodide concentration (Fig. 6). Using the second procedure, the peak area was evaluated by weighing: the peaks recorded on a paper sheet were cut out and weighed on analytical balances. The comparison of both figures gives a more favourable result for the second way

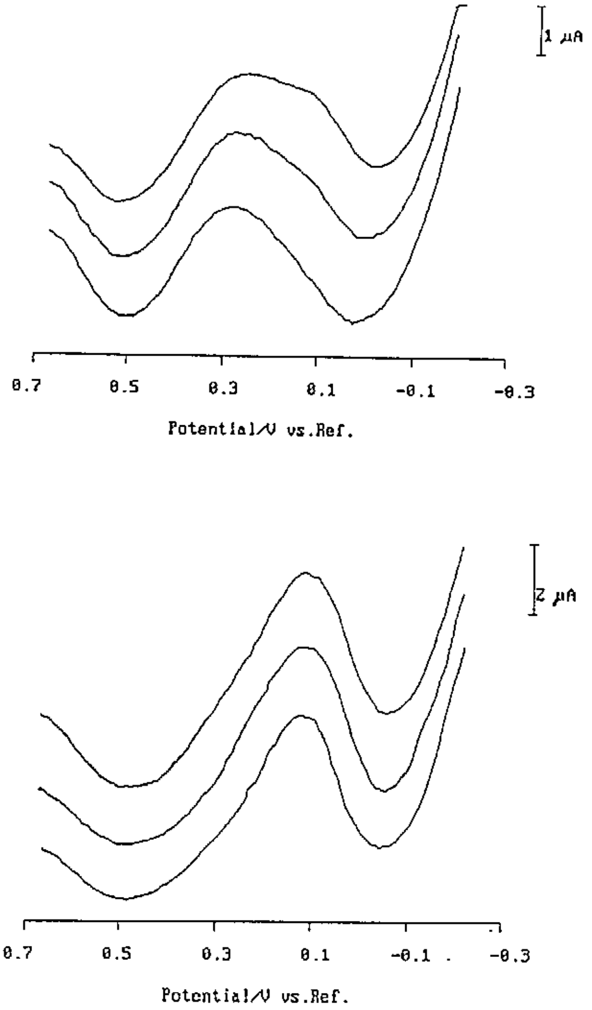

Fig. 3 Typical voltammograms recorded in real samples of table salts: Above - a salt iodinated by addition of KI; Below - a salt iodinated by addition of KIO_3 (reduced before the voltammetric procedure with hydrazine), both with the standard addition of KI. Experimental conditions: PAR 174, deposition time - 1 min, electrolyte - sample solution (10 ml) + 0.2 M HCl (10 ml) + 10^{-4} M KI (200 µl)

of the evaluation, showing more linear dependence on concentration of iodine.

The detection limit for iodide, 2.5×10^{-7} mol l^{-1}, was evaluated *via* 5 independent measurements and then with "3:1 signal to noise" ratio. The reproducibility was determined using a PAR 174A polarographic analyser with a relative error of about 5 %. The same apparatus was used for the evaluation of the recovery parameter which is presented as an interval value from 80 % to 120 % for concentration levels of 5, 20 and 30 mg I^- kg^{-1}. Interferences of other ions, especially halides and pseudohalides, were studied in multiple concentration excess. Only two anions, Br^- and SCN^- in 100-fold and higher excess, interfered.

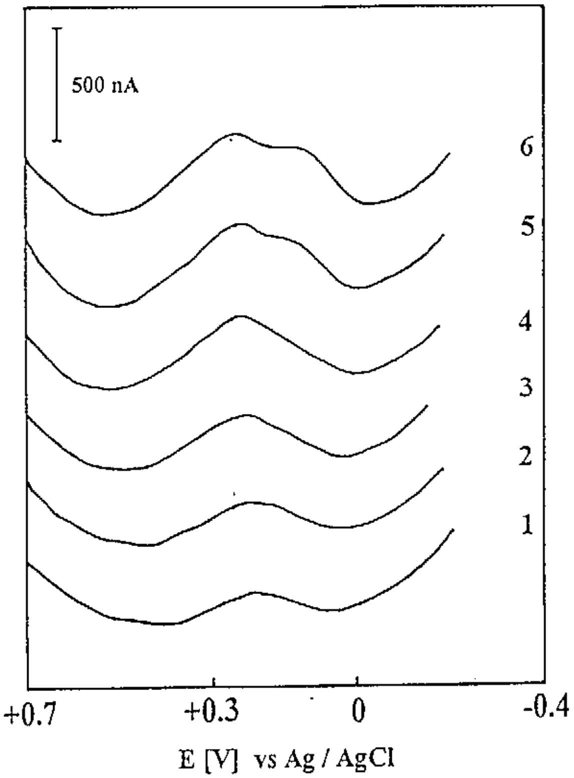

Fig. 4 Calibration voltammograms for concentration range of KI from 5×10^{-7} to 5×10^{-6} mol l^{-1}: Experimental conditions; PA-3, deposition time - 2 min, supporting electrolyte - 0.5 M NaCl + 0.1 M HCl (V = 20 ml). Standard additions of 10^{-4} M KI: (1) 100 µl, (2) 200 µl, (3) 400 µl, (4) 600 µl, (5) 800 µl, (6) 1000 µl

Determination of Iodine Content in Real Samples

Table salts and mineral water were taken as representatives of real samples. The results of analyses are summarized in Table I for both voltammetric and reference methods. The reference analyses were realized by means of iodometric titrations and ICP-MS technique. The results are given in mg I^- kg^{-1} for table salt samples and in mg I^- l^{-1} for a mineral water sample. Taking into account the different principles of the methods used as well as the low concentration level of the species to be determined, the agreement of the results can be considered acceptable.

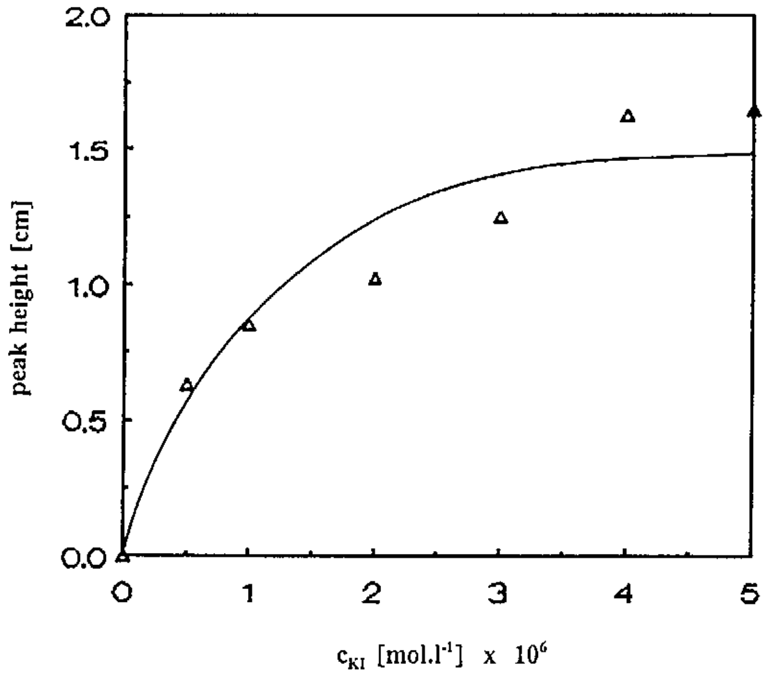

Fig. 5 The dependence of the peak height on concentration of KI

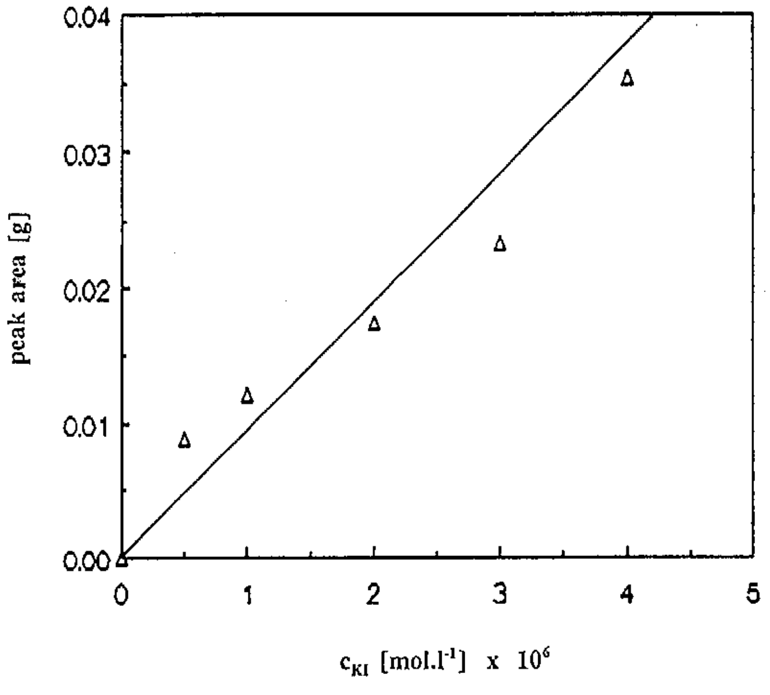

Fig. 6 The dependence of the peak area on concentration of KI

Table I Summarized results of voltammetric and reference determinations of iodide

Sample type		Declared	Determined		
			DPCSV	Iodometric titration	ICP-MS
salt contg. I^- [a]	[a]	15 - 35 [d]	14.9±4.7 [d,f]	21.6 [d]	20.5±1.3 [d,f]
salt contg. IO_3^-	[b]	15 - 25 [d]	22.9±1.7 [d,f]	25.3 [d]	17.1±2.1 [d,f]
mineral water	[c]	7.2 [e]	5.2 [e]	-	-

Specification of the samples: [a]) table salt (Sůl jedlá-jodidovaná, Senquar Litomyšl, CZ); [b]) table salt (Alpská stolní sůl, Bad Reichenhaller, D); [c]) mineral water (Vincentka, Helios Praha, CZ). Expressed as a content of iodide, given in [d]) mg kg^{-1}, [e]) mg l^{-1}; [f]) computed as arithmetic mean ± standard deviation values.

Conclusion

The advantages of the voltammetric method developed and described in this paper can be seen in the following points. First, treatment of samples needs a minimum of manual operations. Secondly, high selectivity is obtained due to the combined accumulation mechanism, allowing to minimize interfering effects of other species. Furthermore, relatively easy preparation of the working electrode should be mentioned. Finally, as appeared during the preliminary measurements in the presence of a cationic surfactant (e.g., Septonex), the sensitivity increase of measurement is possible resulting in a surfactant effect on increasing ion-pairing capabilities of a CPE. This line should be studied in the future work to achieve lower detection limit, which is important for different types of samples containing very low concentrations of iodide.

Acknowledgements

Financial supports of the Grant Agency of the Czech Republic (project No. 203/96/0124) and of the AKTION Austrian-Czech Academic Exchange Program (project No. 5p1) are gratefully acknowledged.

References

1. Ortiz R., de Márquez O., Márquez J.: Anal. Chim. Acta **215**, 307 (1988).
2. Luther G.W., Swartz Ch.B., Ullman W.J.: Anal. Chem. **60**, 1721 (1988).
3. Brainina Z.Kh., Sapozhnikova E.Ya.: Zh. Anal. Khim. **21**, 1342 (1966).

4. Möller A., Scholz F., Lovric M.: Electroanalysis **7**, 987 (1995).
5. Vytřas K., Švancara I.: Chem. Listy **88**, 412 (1994).
6. Kalcher K., Wang J., Kauffmann J.-M., Švancara I., Vytřas K., Neuhold C., Yang Z.P.: Electroanalysis **7**, 5 (1995).
7. Kwak M.-K., Park D.-S., Won M.-S., Shim Y.-B.: Electroanalysis **8**, 680 (1996).
8. Kalcher K.: Fresenius Z. Anal. Chem. **321**, 666 (1985).
9. Švancara I., Vytřas K.: Chem. Listy **88**, 138 (1994).
10. Konvalina J.: *Extraction onto Carbon Paste Electrodes and Its Application to the Determination of Iodine,* MSc Thesis, University of Pardubice, Pardubice 1997.
11. Švancara I., Vytřas K.: Anal. Chim. Acta **273**, 195 (1993).
12. Vytřas K., Švancara I., Renger F., Srey M., Vaňková R., Hvízdalová M.: Collect. Czech. Chem. Commun. **58**, 2039 (1993).
13. Wang J.: *Stripping Analysis,* VCH, Deerfield Beach, 1985