

Introduction

Chlorine is one of the most important raw materials for the chemical industry. In Europe, 10 million tons of chlorine are produced annually by the electrolysis of sodium chloride solutions using predominantly the two-compartment membrane technology.

The membrane process, however, requires highly purified feedstock solutions. One of the most important parameters to be monitored is the concentration of iodide. In the electrolysis cell, iodide is readily oxidized at the anode. The formed oxidation products precipitate inside the ion-exchange membrane and decrease the membrane's useful lifetime.

The most commonly applied analytical methods for determining the iodide ion are voltammetry, ion chromatography, inductively coupled plasma optical emission spectrometry (ICP-OES) and inductively coupled plasma mass spectrometry (ICP-MS). Further methods involve the determination by iodide-selective electrodes or colorimetric detection after upstream reaction with organic compounds.

This work describes the straightforward and cost-efficient determination of iodide after conversion to iodate using differential pulse voltammetry at the hanging mercury drop electrode (HMDE). The concentration of the iodide can be quantified by the calibration curve or the standard addition technique.

System setup: 884 Professional VA



Preparation of the measuring solutions

Measuring solutions

- standard solution: 16 μL iodide solution (50 mg/L) is added to 20 mL supporting electrolyte consisting of 300 g/L NaCl
- salt sample: 0.25 mL sample is added to 19.75 mL supporting electrolyte

Procedure

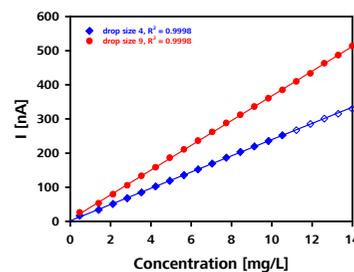
- The pH value of the measuring solution is adjusted to 11...11.5 by adding 20 μL of a 30% NaOH solution.
- After adding 50 μL of a 1 mol/L sodium hypochlorite solution and stirring for 30 s, the reaction solution is allowed to stand for 20 minutes.
- 1 mL of a 10% sodium sulfite solution is added until all hypochlorite is destroyed. A starch solution is used to test for residual iodide.
- After excess hypochlorite is consumed, add 0.1 mL EDTA solution.

Voltammetric parameters

Voltammetric parameters for the iodide determination were optimized in preliminary experiments.

Sample volume	0.20...0.25 mL sample	Calibration technique	Standard addition Calibration curve
pH value	8.5 \pm 0.5 (adjustment with NaOH)	Start potential	-700 mV
Working electrode	Hanging Mercury Drop Electrode (HMDE)	End potential	-1300 mV
Reference electrode	Ag/AgCl/KCl (3 mol/L)	Pulse amplitude	50 mV
Auxiliary electrode	Pt Rod Electrode	Pulse time	40 ms
Measuring mode	Differential pulse	Sweep rate	13 mV/s

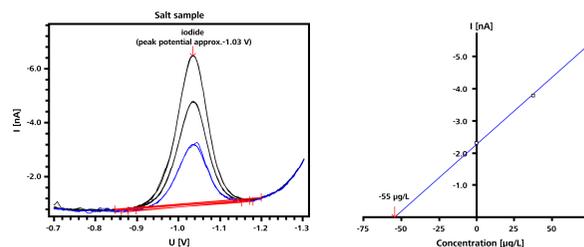
Method characteristics



	Mercury drop size	
	4	9
Linear range up to [$\mu\text{g/L}$]	11000	15000
Limit of detection [$\mu\text{g/L}$]	10.0	2.5
Limit of quantification [$\mu\text{g/L}$]	30.0	10.0

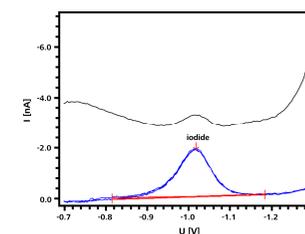
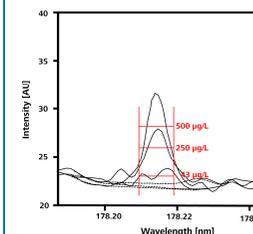
Iodide determination in a salt sample

The voltammogram showed a well-defined peak with a peak potential of -1.03 V. The iodide concentration was determined using the standard addition technique.



Comparison ICP-OES and voltammetry

The iodide content in a brine sample was determined by inductively coupled plasma optical emission spectrometry (ICP-OES) using the most intensive 178.218 nm iodine emission line and by voltammetry.



- moderate limit of detection
- samples have to be stored under acidic conditions
- matrix dependent (e.g., the phosphorus spectral line of 178.222 nm interferes with the most intensive emission line of iodine at 178.218 nm)
- excellent limit of detection
- no sample storage provisions required
- widely matrix independent

Conclusions

In this study, we developed a straightforward and sensitive method for the trace determination of iodide in brine used for chlor-alkali electrolysis. The method involves the oxidation of iodide to iodate and the subsequent determination of the iodate by differential pulse voltammetry. The quantitative iodide conversion to iodate is achieved by treatment with sodium hypochlorite. After 20 minutes reaction time, excess hypochlorite is removed by adding sodium sulfite. Interfering metal traces are complexed by EDTA addition.

The differential pulse voltammogram showed a reproducible iodate peak at a peak potential of -1.03 V versus the Ag/AgCl/KCl (3 mol/L) reference electrode. Iodide concentrations have been analyzed by both the calibration curve and the standard addition technique. However, in terms of matrix effects and feasibility – calibration curves have to be daily registered – we favor the standard addition technique. For mercury drop sizes of 4 and 9, iodide can be determined with a limit of detection of 10 $\mu\text{g/L}$ and 2.5 $\mu\text{g/L}$, respectively. The method is linear over three orders of magnitude and neither high salt nor bromine contents interfere with the iodide determination.

The described differential pulse voltammetric method for the determination of iodide in brine has significant advantages over other commonly employed methods. Besides the excellent price-performance ratio, the voltammetric iodide determination excels by its sensitivity, selectivity and high degree of matrix independence.