

Summary

A convenient adsorptive cathodic stripping voltammetric (AdCSV) method has been developed for trace determination of uranium(VI) in drinking water samples using chloranilic acid (CAA). The presence of various matrix components (KNO_3 , Cl^- , Cu^{2+} , organics) can impair the determination of the uranium-CAA complex. The interferences can be mitigated, however, by appropriate selection of the voltammetric parameters. While problematic water samples still allow uranium determinations in the lower $\mu\text{g/L}$ range, in slightly polluted tap water samples uranium can be determined down to the ng/L range, comparable to the determination by current ICP-MS methods.

Introduction

Uranium is radioactive, toxic, and a suspected teratogen. Several countries of the European Union plan to introduce a legal limit for the maximum concentration of uranium in drinking water. While different national health authorities prescribe limits ranging up to $10 \mu\text{g/L}$, the World Health Organization (WHO) recommends a concentration limit for uranium of $15 \mu\text{g/L}$.

With chloranilic acid (CAA, 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone) as complexing agent, dissolved uranium(VI) can be determined by «*Adsorptive Cathodic Stripping Voltammetry*» (AdCSV) down to the ppt level. The technique is inexpensive and robust; it can be implemented on stand-alone instruments as well as on fully automated voltammetric systems. A validation of the voltammetric method resulted in a limit of detection (LOD) of $0.1 \mu\text{g/L}$ uranium with a relative standard deviation smaller than 3.3%. In Europe a DIN/EN standard for the determination of uranium in mineral and tap water by using this voltammetric technique is under way.

The present work examines the influence of different components of the sample matrix such as organics, copper, and chloride ions.

Principle

Uranium(VI) is preconcentrated as a chloranilic acid complex at $+150 \text{ mV}$ at the hanging mercury drop electrode (HMDE) at a pH of about 2. In the subsequent measurement using AdCSV, a peak cathodic current of the uranium-CAA complex is recorded at approx. -90 mV (vs. $\text{Ag}/\text{AgCl}/3 \text{ mol/L KCl}$). The determination of uranium(VI) is specific and selective, as the positive deposition potential means that other metal-CAA complexes or organic matrix components of natural waters are either not adsorbed at all or hardly adsorbed on the HMDE.

System setup



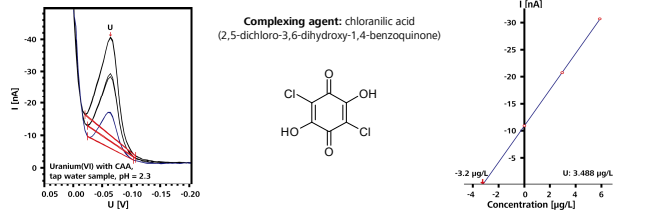
- 797 VA Computrace
- 800 Dosino
- 702 SM Titrino



If a high sample throughput is required, the voltammetric uranium determination can be completely automated. In addition to liquid handling using a sample changer, dosing units, and pumps, the use of a titrator permits to carry out direct pH measurement and adjustment in the voltammetric measuring cell.

U(VI) in a tap water sample

Sample volume	10 mL groundwater or tap water sample	Mode	Differential pulse (DP)
Complexing agent	0.1 mL chloranilic acid (CAA), 0.01 mol/L	Evaluation technique	Standard addition
pH value	2.3 ± 0.3 (adjustment with HNO_3 or KOH)	Deposition	potential $+150 \text{ mV}$ time $10 \dots 120 \text{ s}$
Working electrode	Hanging Mercury Drop Electrode (HMDE)	Potential	start -75 mV end -200 mV
Reference electrode	$\text{Ag}/\text{AgCl}/3 \text{ mol/L KCl}$	Peak potential	$-90 \text{ mV} \pm 50 \text{ mV}$
Auxiliary electrode	Pt or glassy carbon		

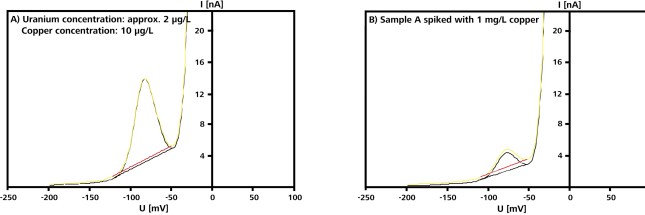


Interferences

a) Too high **chloride concentrations** can interfere with the uranium determination. Together with mercury the chloride forms Hg_2Cl_2 and prevents the deposition of the uranium-CAA complex at the working electrode. This process greatly depends on the pH and the deposition potential. By optimization of the pH and the deposition potential, uranium can still be detected in the lower $\mu\text{g/L}$ range, even with a chloride content as high as 5 g/L .

Chloride concentration in sample vessel [mg/L]	Deposition potential [mV]	
	5 $\mu\text{g/L}$ standard	0.5 $\mu\text{g/L}$ standard
	+150	+100
500	●	●
1000	●	●
1500	●	●
2000	●	●
2500	●	●
3000	●	●
4000	●	●
5000	●	●

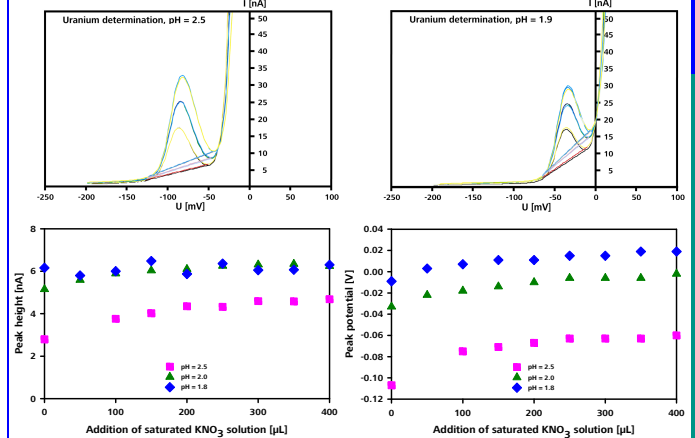
b) High **copper contents** in the sample reduce the sensitivity of the uranium determination. Using the standard addition method, comparable uranium contents are obtained, both in the presence and absence of Cu^{2+} ions. Uranium can be accurately determined up to a copper concentration of 1 mg/L without any sample preparation being required.



c) In order to estimate the **influence of organics**, samples with different TOC (total organic carbon) contents were measured and the recovery of a spiked uranium standard was determined. In the presence of 7 mg/L TOC, recovery rates for spiked samples are in the range between 70 and 120%. Water samples with higher TOC contents ($>10 \text{ mg/L}$) require one of the sample preparation techniques stipulated by DIN 38406-17.

Influence of pH and KNO_3 concentration

An alteration of the pH value and/or the KNO_3 concentration influences the potential value and the signal height of the uranium-CAA signal. The addition of KNO_3 is very helpful if the samples have differing ionic strengths. However, at low pH values a too high KNO_3 concentration shifts the uranium-CAA signal too far in the anodic direction, so that the evaluation becomes more difficult, particularly with high chloride contents.

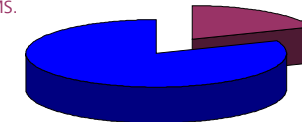


Comparative AdCSV-ICP/MS measurements

A comparison of the measured values obtained with ICP/MS and AdCSV shows that on average a lower uranium content is determined by voltammetry than by ICP/MS. This varies from laboratory to laboratory, e.g. due to differing calibrations of the ICP-MS instruments:

Laboratory	No. of determinations	Uranium concentration (AdCSV) < Uranium concentration (ICP/MS)
1	7	5
2	8	6
3	11	10

19% of the uranium concentrations determined by AdCSV exceed those determined by ICP/MS.



81% of the uranium concentrations determined by AdCSV are lower than those determined by ICP/MS.

References

- (1) S. Sander and G. Henze, Adsorption voltammetric techniques for the determination of uranium(VI) with 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone as complex forming agent, Fresenius Journal of Analytical Chemistry, **349**, 654-658 (1994).