Metrohm

Application Bulletin 430/1 e

Determination of uranium by adsorptive stripping voltammetry according to DIN 38406-17

Summary

This Application Bulletin describes the methods for the determination of uranium by adsorptive stripping voltammetry (AdSV) according to DIN 38406 part 17. The method is suitable for the analysis of ground, drinking, sea, surface and cooling waters, in which the concentration of uranium is of importance. The methods can, of course, also be used for the trace analysis in other matrices.

Uranium is determined as chloranilic acid complex. The limit of detection in samples with low chloride concentration is about 50 ng/L and in seawater about 1 µg/L. Matrices with high chloride content can only be analyzed after reduction of the chloride concentration by means of a sulfate-loaded ion exchanger.

Instruments

VA instrument capable of operating a Multi-Mode Electrode and supporting differential pulse (DP) measuring mode	
909 UV Digester	2.909.0014

Electrodes

WE	Multi-Mode Electrode pro Mercury drop capillary	6.1246.120 6.1226.030 or 6.1226.050
RE	Ag/AgCl reference electrode Ag/AgCl/KCl (3 mol/L) Electrolyte vessel Filled with c(KCl) = 3 mol/L	6.0728.x20 6.1245.010
AE	Pt rod electrode	6.0343.x00

Reagents

All of the used reagents must be of purest quality possible (for analysis or for trace analysis*).

- Chloranilic acid (2,5- dichloro-3,6-dihydro-1,4-benzoquinone), for analysis, CAS 87-88-7
- Potassium nitrate, KNO_3, for trace analysis*, CAS 7757-79-1
- Potassium hydroxide solution, w(KOH) = 30%, for trace analysis*, CAS 1310-58-3
- Nitric acid, $w(HNO_3)$ = 65%, for trace analysis*, CAS
- U standard stock solution, β(U) = 1 g/L (commercially available)
- Ultrapure water, resistivity >18 MΩ·cm (25 °C), type I grade (ASTM D1193)

* e.g., Merck suprapur®, Honeywell Fluka TraceSelect® or equivalent

Solutions

CAA solution	c(chloranilic acid) = 0.01 mol/L 0.209 g chloranilic acid are dissolved and filled up to 100 mL with ultrapure water.
KNO_3 solution	$c(KNO_3)$ = 1 mol/L 10.11 g KNO_3 are dissolved and filled up to 100 mL with ultrapure water.
Diluted HNO_3 solution	$c(HNO_3)$ = 1.45 mol/L 10 mL HNO_3 are diluted to 100 mL with ultrapure water.
Diluted KOH solution	w(KOH) ≈ 10% (c(KOH) = 1.78 mol/L) 10 g KOH solution are dissolved and filled up to 100 mL with ultrapure water.

Standard solutions

U standard solution	β(U) = 1 mg/L The standard stock solution is diluted with $c(HNO_3)$ = 0.014 mol/L.

Sample preparation

- Ground water, surface waters, mineral waters and drinking waters can usually be analyzed without pre-treatment.

Organic matter often interferes with voltammetric determinations and therefore sample solutions usually have to be digested.

- Low polluted waste waters can be digested with the 909 UV Digester.
    - Add 50 - 100 µL w(H_2O_2) = 30% and 10 µL w(HCl) = 30% to 10 mL acidified sample (pH = 2) and irradiate for 90 min at 90 °C. After cooling to room temperature, the digested sample can be transferred directly to the polarographic vessel.
- Samples with organic matter (foods, pharmaceuticals etc.) must be digested.
    - High-pressure asher
    - Microwave digestion

  Both techniques oxidize the samples in a closed digestion vessel by means of a mixture of concentrated mineral acids.

Analysis

Measuring solution

10 mL (diluted) sample

1 mL KNO_3 solution

0.1 mL CAA solution

Adjust the pH value to 2.3 ± 0.3 with diluted KOH or HNO_3.

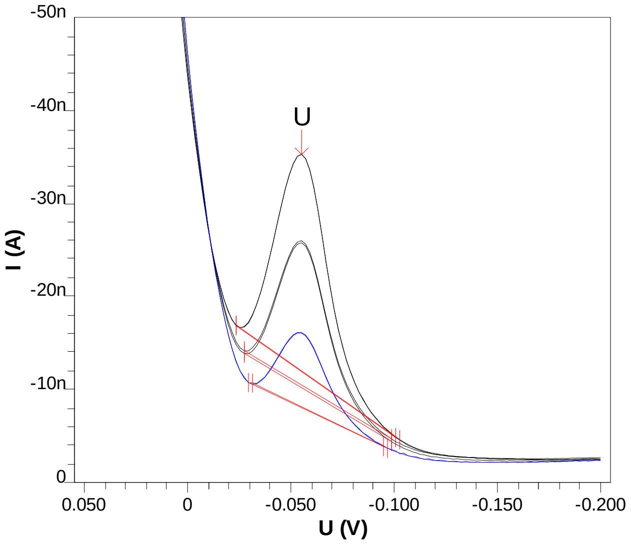
The concentration is determined by standard addition.

Parameters

Voltammetric	
Electrode operating mode	HMDE
Measuring mode	DP – Differential pulse
Stirring rate	2000 min^{-1}
Potentiostatic pretreatment	
Potential 1	0.15 V
Waiting time 1	60 s
Equilibration time	5 s
Sweep	
Start potential	0.05 V
End potential	-0.2 V
Potential step	0.002 V
Potential step time	0.1 s
Sweep rate	0.02 V/s
Pulse amplitude	0.05 V

Substance	
Name	U
Characteristic potential	-0.05 V

Example



```
U
c =     1.986 ug/L
+/-     0.023 ug/L (1.18%)
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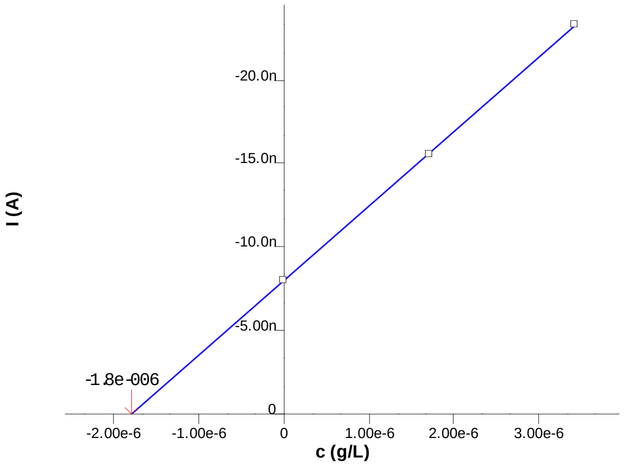

Result

Sample	Drinking water
Sample size	10.0 mL
β(U)	2.0 µg/L

Comments

- The peak potential of the U-CAA complex depends on the pH and varies between -0.02 V (pH 1.8) and -0.12 (pH 2.8).

- High chloride concentrations interfere with the determination due to the formation of Hg_2Cl_2.
- Cu does not interfere up to a concentration of 1 mg/L.
- Mo, Sb, Sn and V form CAA complexes as well. These do not interfere with the determination, but require the addition of more CAA solution.
- For the determination of very low uranium concentrations the time for deposition (Waiting time 1) can be increased to e.g. 180 s.
- The steep drop of the background current at positive potentials relates to the presence of chloranilic acid. If very small uranium signals have to be evaluated, it is sometimes beneficial to reduce the CAA concentration in the measuring solution to also reduce the current drop.
- The uranium concentration in the vessel should not exceed 50 µg/L (with standard additions). If concentrations are higher, either the sample must be diluted or the analysis must be done at the SMDE.
- Higher uranium concentrations also require more CAA.

References

- DIN 38406-17 Determination of uranium – Method using adsorptive stripping voltammetry in surface water, raw water and drinking water
- Henze G., Sander S., Adsorption voltammetric techniques for the determination of uranium(VI) with 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone as complex forming reagent, Fresenius J. Anal. Chem. (1994) 349:654-658
- Henze G., Sander S., Wagner W., Direct Determination of Uranium Traces by Adsorptive Stripping Voltammetry, Universitäten Kaiserslautern und Trier 1994
- Henze G., Sander S., Chloranilsäure als Komplexbildner für die Ultraspurenanalyse von Elementen durch Adsorptions-Stripping-Voltammetrie, GIT Fachz. Lab. 12/96
- Van den Berg, C. M. G., Potentials and potentialities of cathodic stripping voltammerty of trace elements in natural waters, Anal. Chim. Acta (1991) 250: 265-276
- Metrohm Application Bulletin 113

Appendix

Report for the example determination of uranium in drinking water

```
======== METROHM 797 VA COMPUTRACE (Version 1.3.0.77) (Serial No. 2173) ========
 Determination  : 0704301512_Probe 1.dth
 Sample ID      : Probe 1
 Creator method : bo                  Date : 2007-04-30           Time:  15:12:23
 Creator determ.:                     Date : 2007-07-05           Time:  13:10:47
 Modified by    : ---                 Date :                      Time:
---------------------------------------------------------------------------------
 Method         : Porbe 1.mth
 Title          : Det U
 Remark1        : 10 ml water + 1 ml KNO3+ 0.1 ml CA Merck
 Remark2        :
---------------------------------------------------------------------------------
 Sample amount  :  10.000 mL
 Cell volume    :  11.140 mL
---------------------------------------------------------------------------------
 Substance      : U
 Conc.          :   1.782 ug/L
 Conc.dev.      :   0.021 ug/L     ( 1.18%)
 Amount         :  19.857 ng
 Add.amount     :  19.140 ng

 VR     V       nA      I.mean  Std.Dev.  I.delta   Comments
 -----  ------  ------  ------  --------  --------  ----------------------
 1 - 1  -0.055   -8.00   -8.00     0.005      0.00
 1 - 2  -0.055   -8.00
 2 - 1  -0.055  -15.52  -15.55     0.042     -7.55
 2 - 2  -0.055  -15.58
 3 - 1  -0.055  -23.34  -23.32     0.030     -7.77
 3 - 2  -0.055  -23.30


 Substance    Calibr.      Y.reg/offset        Slope Mean deviat. Corr.Coeff.
 ------------ ------------ ------------ ------------ ------------ ------------
 U            std.add.      -7.968e-009  -4.470e-003   1.087e-010      0.99995

 Solutions
---------------------------------------------------------------------------------

  No. Content                                        Predose (mL)
  --- ------------------------------------------------ ------------
   1  U std 0.957ppm                                 -------


 Final results                         +/- Res. dev.   %     Comments
-----------------------------------    ------------------    -------------------

 U:
 default           =    1.986  ug/L    0.023        1.181
```

Method print for the determination of uranium according to DIN 38406-17

```
---------------------------------------------------------------------------------
 Method parameters
---------------------------------------------------------------------------------
Method          : AB430 Det of U.mth
Title           : Determination of uranium acc. to DIN 38406-17
Remark1         : 10 mL sample + 1 mL KNO3 + 0.1 mL CAA
Remark2         : --> pH 2.3 ± 0.3

Calibration     : Standard addition
Technique       : Batch
Addition        : Manual

Sample ID       : Sample
Sample amount (mL): 10.000
Cell volume (mL): 11.100

Voltammetric parameters
---------------------------------------------------------------------------------
Mode                               : DP - Differential Pulse

Highest current range              : 100 nA
Lowest current range               : 100 nA

Electrode                          : HMDE
Drop size (1..9)                   : 4
Stirrer speed (rpm)                : 2000
```

```
Initial electr. conditioning       : No

No. of additions                   : 2
No. of replications                : 2

Measure blank                      : No
Addition purge time (s)            : 20

Initial purge time (s)             :      300

Conditioning cycles
Start potential (V)                :    0.000
End potential (V)                  :    0.000
No. of cycles                      :        0

Hydrodynamic (measurement)         :      No
Cleaning potential (V)             :    0.000
Cleaning time (s)                  :    0.000
Deposition potential (V)           :    0.150
Deposition time (s)                :   60.000

Sweep
Equilibration time (s)             :    5.000
Start potential (V)                :    0.050
End potential (V)                  :   -0.200
Voltage step (V)                   :    0.002
Voltage step time (s)              :    0.100
Sweep rate (V/s)                   :    0.020
Pulse amplitude (V)                :    0.050
Pulse time (s)                     :    0.040

Cell off after measurement         :      Yes

Peak evaluation
--------------------------------------------------------------------------------
Regression technique               : Linear Regression
Peak evaluation                    : Height
Minimum peak width (V.steps)       : 5
Minimum peak height (A)            : 1.000e-010
Reverse peaks                      : No
Smooth factor                      : 4
Eliminate spikes                   : Yes

Substances
--------------------------------------------------------------------------------
U                         : -0.040 V   +/- 0.050 V

Standard solution         : 1   1.000 mg/L
Addition volume (mL)      : 0.020

Uranium                   : Final result (U) =
                            Conc * (11.1 / 10) * (1e+006 / 1) + 0 - 0

Baseline
--------------------------------------------------------------------------------
Substance Addition    automatic start (V) end (V) type        scope
--------------------------------------------------------------------------------
U         Sample      yes       ---       ---     linear      wholePeak
          Addition 1  yes       ---       ---     linear      wholePeak
          Addition 2  yes       ---       ---     linear      wholePeak
--------------------------------------------------------------------------------
```