

Adsorption voltammetric techniques for the determination of uranium(VI) with 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone as complex forming reagent

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Abstract. Uranium(VI) can be determined by adsorptive voltammetric techniques, as its chloranilic acid complex, over a wide concentration range. Differential pulse polarography is useful for quantification of uranium between 0.1 and 1.5 mg/l; for the range from 10 to 500 $\mu\text{g/l}$ differential pulse voltammetry and for ultra-trace analysis between 0.024 and 40 $\mu\text{g/l}$ adsorptive stripping voltammetry are preferred. The standard deviation for the 3σ -detection limit of 24 ng/l uranium was found to be 8%. In the trace analysis of metals in aquatic environmental systems by adsorptive stripping voltammetry it is normally necessary to decompose polluted water samples by UV irradiation or microwave digestion. The advantage of the developed method is the fact that no sample pretreatment is necessary.

Introduction

The uranium content of water samples covers a wide range from ng/l in natural waters up to mg/l concentrations in waste water. Unnaturally high concentrations of uranium can be caused by nuclear and mining industry.

Various spectroscopic methods are important for the determination of traces of uranium. In addition to their expensive instrumentation, however, these methods often require a pre-concentration step because of matrix influences or inadequate detection limits. Because of its higher sensitivity, the determination of uranium by neutron activation analysis is more attractive. However the specialized instrumentation, indispensable skills, time and high costs limit its use. The comparably high sensitivity of voltammetric techniques, such as various forms of stripping voltammetry, enable the quantification of uranium with relatively simple and less expensive methods.

Voltammetric methods are mainly controlled by the reduction of uranium(VI) to uranium(V). Using dp-

polarography, detection limits were found to be in the lower mg/l-level [1]. Anodic stripping voltammetry with amalgam accumulation is inefficient for the determination of uranium traces because of the electrochemical behaviour and the low solubility of uranium in mercury [2]. However adsorptive stripping voltammetry is a powerful technique useful for uranium trace analysis.

Adsorption voltammetry is a technique in which the analyte is preconcentrated first by adsorption onto a mercury drop or film as the working electrode followed by voltammetric measurements of the electroactive species. This method has been applied to the stripping voltammetric determination of uranium in the presence of complex forming agents such as pyrocatechol [3, 4], oxine [5, 6], mordant blue [7, 8], cupferron [9], diisopropylmethylphosphate [10], triisobutylphosphate and tripropylphosphate [11, 12] and 4-(5-Brom-2-pyridylazo)-N,N-diethyl-3-hydroxyanilin [13].

In order to determine uranium more sensitively and selectively, several new complexing agents were tested. As a result of these investigations 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone (chloranilic acid) has been found to form a uranium complex which was particularly useful for higher selectivity in the adsorption and for better reproducibility in the determination step [15].

Based on the formation of this complex the procedure developed covers, using the techniques of the differential pulse polarography (DPP), differential pulse voltammetry (DPV) and adsorptive stripping voltammetry (AdSV), the whole concentration range of interest from the mg/l to the ng/l range.

The procedure has been applied to the determination of uranium traces in river water und mining waste water. Interferences caused by metals and organic substances have been studied.

Experimental

Apparatus and reagents

Voltammetric and polarographic measurements were performed using a Metrohm VA processor 693 in conjunc-

tion with the 694 VA stand; this includes a multi-mode electrode and makes possible the reproducible production of a static mercury drop (SMDE) and a hanging mercury drop as the working electrode (HMDE). The three-electrode system was completed by a Ag/AgCl (3 mol/l KCl) reference electrode and a glassy carbon auxiliary electrode.

All measurements were carried out using the differential pulse mode with a -50 mV pulse amplitude.

A MDS 2000 microwave digestion system (CEM Corporation, NC, USA), controllable between 0% and 100% of full power (700 W) and a UV Digester 705 (Fa. Metrohm) were used for the oxidative decomposition of interfering organic compounds in natural water samples. Using microwave high pressure oxidative digestion, sample treatment was carried out in the Teflon PFA[®] decomposition vessels after addition of 125–500 mg Oxisolv[®] (Fa. Merck) as oxidizing agent to 20 ml of each sample. For the UV digestion, 100 μ l H₂O₂ was added to a 10 ml water sample.

All chemicals used were of analytical reagent grade (Merck and Fluka). A stock solution with 1 g/l uranium was prepared by dissolving 1.78 g (CH₃COO)₂UO₂·2H₂O in 1 l of water containing 1 ml HNO₃ (65%). The concentration of the chloranilic acid solution was 5×10^{-3} mol/l. pH-values were adjusted with HCl and NaOH of suprapure quality. The water used was obtained from a Millipore Milli-Q system. The samples were deaerated with argon.

Results and discussion

Determination by AdSV and DPV

The principle of the determination is to preconcentrate uranium(VI) from the sample solution as the chloranilic acid complex, potentiostatically on a hanging mercury drop and subsequently to dissolve it again by applying a cathodic potential scan.

A peak occurs in the voltammogram as a result of the reduction of uranium(VI); this can be evaluated quantitatively. For each step of the procedure, the optimum working conditions had to be ascertained with regard to the composition of the basic electrolyte and to the conditions for potentiostatic preconcentration.

Figure 1 shows how the height and the potential of the AdSV peaks depend on the pH-value of the sample solution. The peak shifts to more negative potentials and is reduced in size with increasing pH-value. The best results with regard to good reproducibility of the peak were obtained in a solution adjusted with hydrochloric acid to pH 2.5. The peak potential under these conditions was found to be between -100 and -120 mV.

The sensitivity of the determination of metal traces by AdSV also depends on the concentration of the complex-forming agent. At a concentration of 0.3×10^{-4} mol/l chloranilic acid, the maximum peak height is obtained in a 4 μ g/l uranium-containing sample solution (Fig. 2). Higher concentrations of chloranilic acid do not increase the peak height but are necessary for the determination

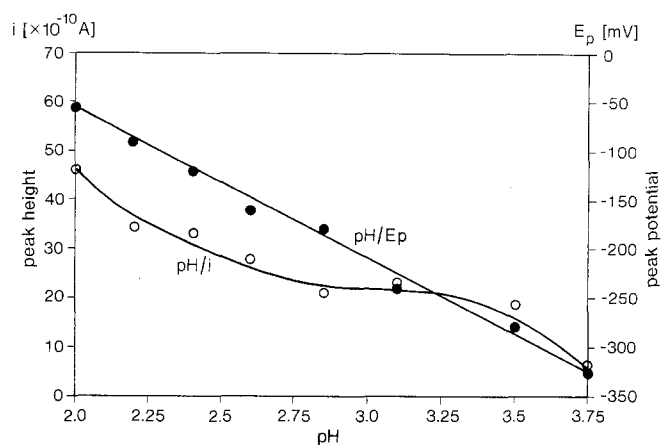


Fig. 1. Dependence of peak height (\circ) and peak potential (\bullet) on pH-value. Conditions: 4 μ g/l U(VI); 2.5×10^{-4} mol/l chloranilic acid; $E_{\text{acc}} = +150$ mV; $t_{\text{acc}} = 1$ min

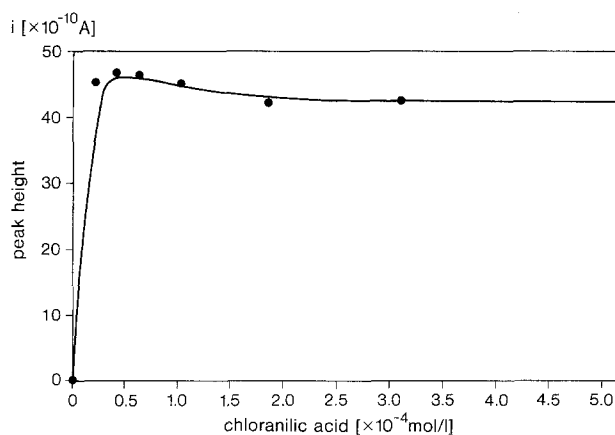


Fig. 2. Effect of the chloranilic acid concentration on the peak height. Conditions: 4 μ g/l U(VI); pH 2.5; $E_{\text{acc}} = 150$ mV; $t_{\text{acc}} = 1$ min

of higher uranium contents. Therefore all further investigations were carried out in the presence of 2.5×10^{-4} mol/l chloranilic acid.

The accumulation potential (E_{acc}) is a further parameter which has to be optimized to increase sensitivity and selectivity in AdSV. In a solution with pH 2.5, with 2.5×10^{-4} mol/l chloranilic acid and 4 μ g/l uranium(VI), no essential change in peak height was observed at pre-concentration potentials between $+50$ and $+150$ mV (Fig. 3). Because of the selectivity in adsorption further investigations were carried out at a pre-concentration potential of $+150$ mV.

Figure 4 demonstrates the dependence of the peak height on the accumulation time (t_{acc}). The peak height increases almost linearly for the first 7 min of preconcentration, but does then not change substantially with longer pre-concentration times. Representative stripping voltammograms obtained at different accumulation times are given in Fig. 5. The front overlap of the uranium peak is caused by the chloranilic acid signal but does not affect the evaluation of the voltammograms.

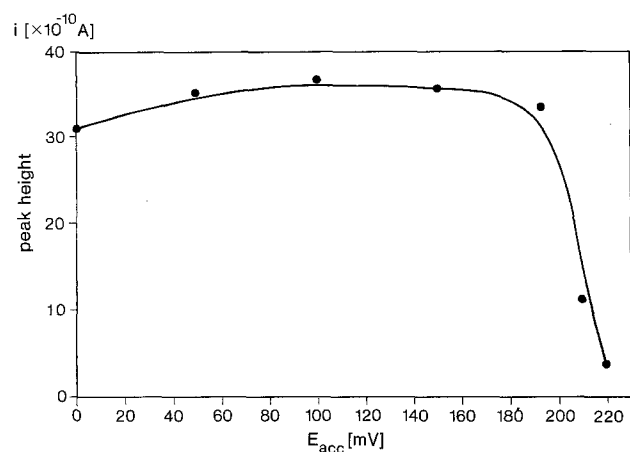


Fig. 3. Peak height in dependence on the accumulation potential. Conditions: $4 \mu\text{g/l}$ U(VI); 2.5×10^{-4} mol/l chloranilic acid; pH 2.5; $t_{\text{acc}} = 1$ min

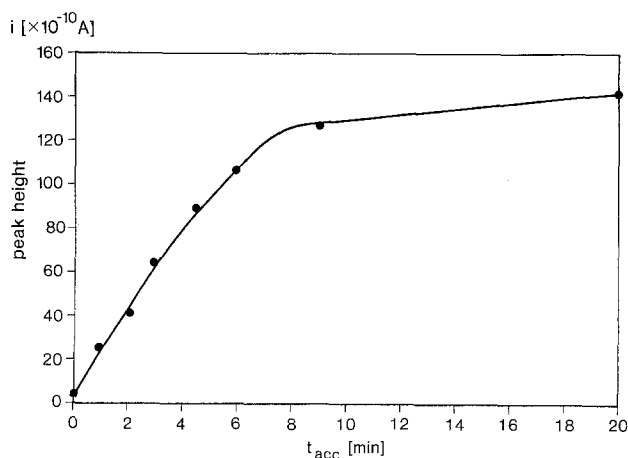


Fig. 4. Peak height in dependence on the accumulation time. Conditions: $4 \mu\text{g/l}$ U(VI); 2.5×10^{-4} mol/l chloranilic acid; pH 2.5; $E_{\text{acc}} = +150$ mV

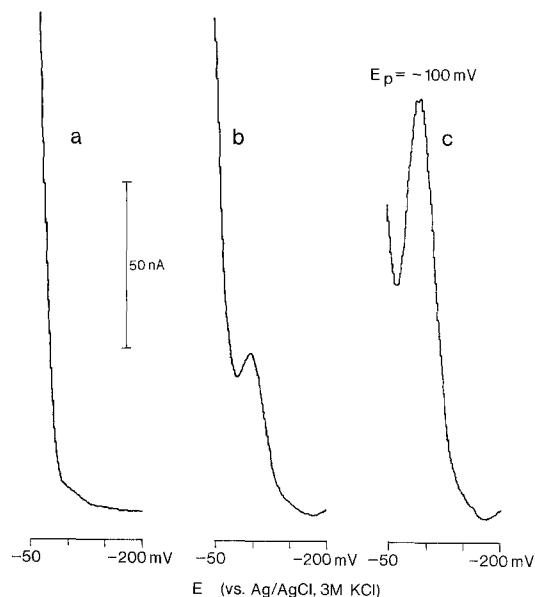


Fig. 5a-c. Adsorptive stripping voltammogram at different accumulation times. Conditions: $4 \mu\text{g/l}$ U(VI); 2.5×10^{-4} mol/l chloranilic acid; pH 2.5; $E_{\text{acc}} = +150$ mV. t_{acc} : 0 s (a); 60 s (b); 250 s (c)

The linear concentration range for the determination of uranium by AdSV was found to be between 0.024 and $10 \mu\text{g/l}$ uranium(VI) using an accumulation time of 7 min at an accumulation potential of +150 mV, a pH-value of 2.5 and a chloranilic acid concentration of 2.5×10^{-4} mol/l. The standard deviation for the 3σ -detection limit of 24 ng/l U(VI) was found to be 8%. The linear range extends to $40 \mu\text{g/l}$ uranium(VI) when the preconcentration time is reduced to 90 s. Without preconcentration (as according to the method of DPV) the linear range extends to $500 \mu\text{g/l}$. Representative differential pulse voltammograms and the calibration plot up to $175 \mu\text{g/l}$ uranium are shown in Fig. 6.

Determination by differential-pulse-polarography (DPP)

Generally the sensitivity of polarographic determination can be improved if the analyte to be determined forms adsorbable complexes. In the case of the polarographic determination of uranium, an increase in sensitivity could be achieved by addition of chloranilic acid to the supporting electrolyte solution. The investigations were performed with a static mercury drop electrode (SMDE) under the same conditions developed for the determination by AdSV and DPV and result in a well defined polarographic peak at -180 mV; the determination range lies between 0.1 mg/l and 1.5 mg/l . Examples of the dp-polarograms and the calibration plot are illustrated in Fig. 7.

Choice of method to be used under different analytical conditions

The results of the investigation show that uranium can be determined over the wide concentration range from 0.024 to $1500 \mu\text{g/l}$. Which polarographic or voltammetric tech-

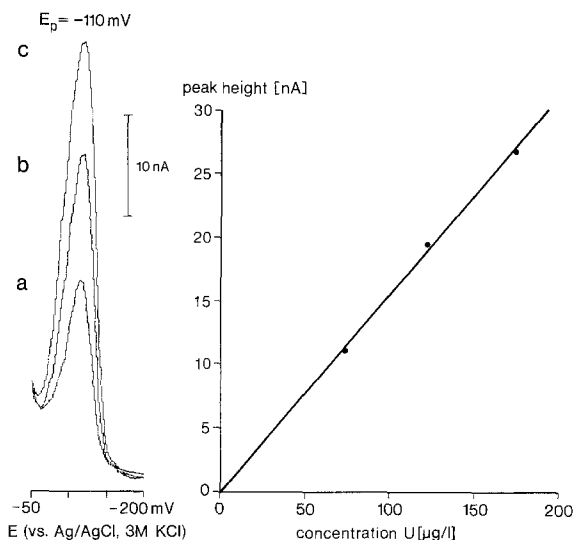


Fig. 6a-c. dp-Voltammograms and calibration plot for the determination of uranium in presence of chloranilic acid using HMDE. Conditions: 2.5×10^{-4} mol/l chloranilic acid, pH 2.5. Uranium concentrations: $75 \mu\text{g/l}$ (a), $125 \mu\text{g/l}$ (b), $175 \mu\text{g/l}$ (c)

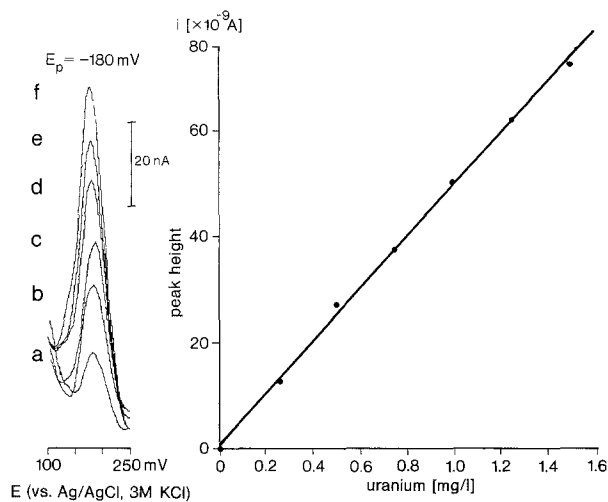


Fig. 7a–f. dp-Polarograms and calibration plot for the determination of uranium in presence of chloranilic acid. Conditions: 2.5×10^{-4} mol/l chloranilic acid, pH 2.5. Uranium concentrations: 0.25 mg/l (a), 0.50 mg/l (b), 0.75 mg/l (c), 1 mg/l (d), 1.25 mg/l (e), 1.5 mg/l (f)

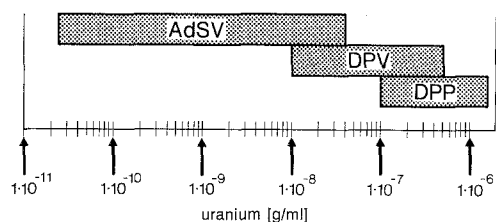


Fig. 8. Concentration ranges for the determination of uranium(VI) by different adsorption voltammetric techniques

nique should be used depends on the concentration of uranium in the sample. As shown in Fig. 8, AdSV, with a pre-concentration period of several minutes, could be used for determinations between 0.024 to 40 $\mu\text{g/l}$ uranium(VI). Using the technique of DPV, the determination range of 40 to 500 $\mu\text{g/l}$ was achieved. Up to 1500 $\mu\text{g/l}$, DPP is the technique of choice.

The techniques developed allow the direct determination of uranium in all natural waters investigated, including polluted surface water, without digestion of the sample; this digestion is necessary for the application of all other well known uranium determinations using voltammetry and polarography. Therefore the described procedures are very efficient and of great advantage for routine work.

Interferences

The voltammetric and polarographic determination of uranium in the presence of chloranilic acid is highly selective and sensitive. Only molybdenum, antimony, tin, vanadium and tungsten also form adsorbable complexes with this agent. Because of differences in their peak potentials, these metals do not interfere with the determination of uranium [14].

High iron contents strongly depress the uranium peak; however the determination of uranium is possible up to a ratio of $[\text{Fe}]/[\text{U}] \leq 1000$. Triton-X-100, a non-ionic tenside, increases the determination of uranium by 100%, when the Triton-X-100 concentration is higher than 1.2 mg/l (Fig. 9). This behaviour of Triton-X-100 is different from that with other metals.

Low concentrations of humic acid depress the uranium signal; concentrations above 10 mg/l increase the signal so that it exceeds the signal of an unpolluted sample at a concentration of 250 mg/l (Fig. 10).

Application

Water samples of different origins were used to test the applicability of the developed techniques to determine uranium. For this purpose the results obtained using chloranilic acid as complexing agent were compared with those obtained by AdSV or DPV using pyrocatechol [3] (Table 1). The investigations showed that, in using pyrocatechol which is known as a wide-band complexing agent, the uranium signal is interfered with by numerous elements and organic compounds; this is not found with the application of chloranilic acid.

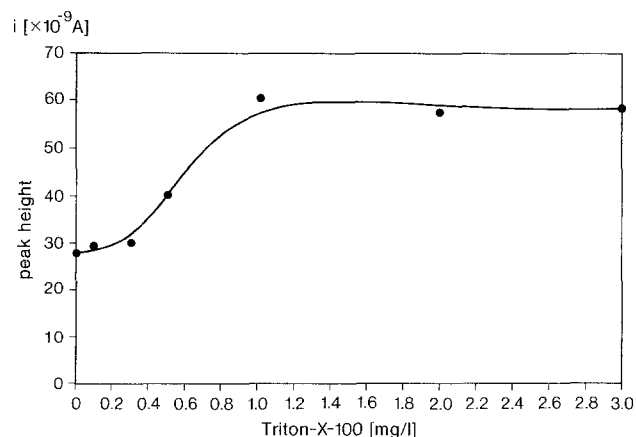


Fig. 9. Influence of Triton-X-100 on the determination of uranium by AdSV. Conditions: 4 $\mu\text{g/l}$ uranium; 2.5×10^{-4} mol/l chloranilic acid, pH 2.5; $t_{\text{acc}} = 90$ s

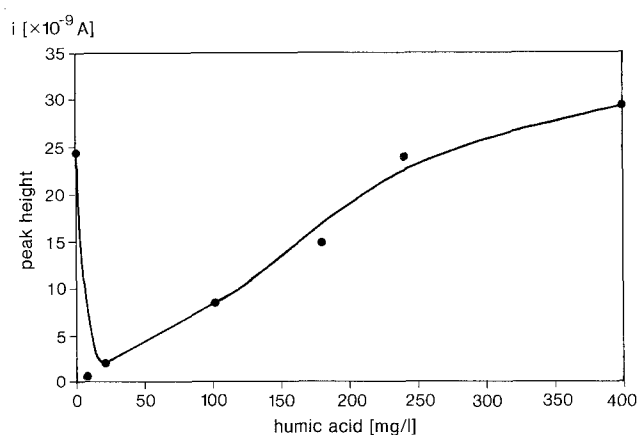
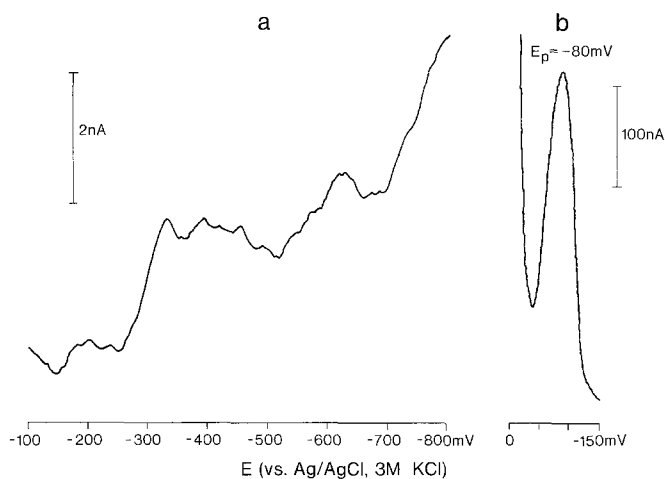


Fig. 10. Influence of humic acid on the determination of uranium by AdSV. Conditions: AdSV; 4 $\mu\text{g/l}$ uranium; 2.5×10^{-4} mol/l chloranilic acid, pH 2.5; $t_{\text{acc}} = 90$ s

Table 1. Determination of uranium in water samples by adsorption voltammetric techniques

Sample	Mode	Electrolyte	Sample pretreatment	t_{acc} (s)	Content ($\mu\text{g/l}/\text{SD}$)
1	AdSV	2.5×10^{-4} mol/l CAA pH 2.5, $E_{acc} = 0.15$ V	–	90	0.572 \pm 0.079 (18.6%)
			Microwave	90	0.572 \pm 0.149 (26%)
			UV	90	0.475 \pm 0.053 (11%)
	AdSV	1×10^{-4} mol/l PC pH 4.5, $E_{acc} = -0.28$ V	–	90	a
			Microwave	90	a
			UV	90	a
2	DPV	2.5×10^{-4} mol/l CAA pH 2.5	–	0	1030 \pm 174 (17%)
			Microwave	0	917 \pm 59 (6.45%)
			UV	0	889 \pm 57 (6.39%)
	DPV	1×10^{-4} mol/l PC pH 4.5	–	0	a
			Microwave	0	a
			UV	0	943 \pm 183 (19%)
3	DPV	2.5×10^{-4} mol/l CAA pH 2.5	–	0	11.5 \pm 1.33 (12.9%)
			Microwave	0	12.79 \pm 1.61 (12.6%)
			UV	0	12.54 \pm 0.976 (7.78%)
	AdSV	1×10^{-4} mol/l PC pH 4.5, $E_{acc} = -0.28$ V	–	90	12.81 \pm 2.12 (16.6%)
			Microwave	90	17.79 \pm 2.27 (12.7%)
			UV	90	15.99 \pm 0.997 (6.2%)

CAA, Chloranilic acid; PC, pyrocatechol

^a Uranium determination was not possible**Fig. 11 a, b.** Voltammograms of the uranium determination in an untreated river water sample (sample 2) in Table 1. **a** dp-Voltammogram obtained after addition of 1×10^{-4} mol/l pyrocatechol (pH 4.5). **b** dp-Voltammogram obtained after addition of 2.5×10^{-4} mol/l chloranilic acid (pH 2.5)

For the determination of uranium in polluted water samples using pyrocatechol, a decomposition of the sample by UV-irradiation or by oxidative microwave decomposition has shown to be necessary.

Sample 1 represents a river water with a natural uranium content. When comparing the results in Table 1 it can be seen that no sample preparation is necessary when chloranilic acid is used as complexing agent. It is not possible to determine uranium in this sample using pyrocatechol even after decomposition.

Sample 2 is taken from a river in the vicinity of a uranium mine; it contains about 1 mg/l uranium, which

was determined by dp-voltammetry. The results of a decomposed and an untreated sample compare well if chloranilic acid is used. When using pyrocatechol as a complexing agent, UV-decomposition is necessary. The experimental results are shown in Fig. 11.

Sample 3 is drainage water from a uranium slagheap. The results of the voltammetric determination using chloranilic acid, with and without sample decomposition, are in good agreement. The mean value was calculated to $12.27 \pm 1.3 \mu\text{g/l}$. The accuracy of this value was proved by neutron activation analysis. With this reference method, $11 \pm 2 \mu\text{g/l}$ uranium were found. The mean content of uranium found in this sample by AdSV using pyrocatechol as complexing agent differs from these values and was found to be $15.5 \pm 1.8 \mu\text{g/l}$ (Table 1).

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