

## A COMPARISON OF SPECTROPHOTOMETRIC METHODS FOR THE DETERMINATION OF URANIUM

Luděk JANČÁŘ, Irena JANČÁŘOVÁ and Josef HAVEL

*Department of Analytical Chemistry, Masaryk University, 611 37 Brno*

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Some spectrophotometric and extraction photometric methods for the determination of uranium were compared using pure solutions, a model sample and samples of surface waters and waste waters; the characteristics examined included sensitivity, accuracy, repeatability, time demands and tediousness. Among the most sensitive methods are those based on the use of triphenylmethane dyes in the presence of surfactants; uranium is separated from associate ions by extraction into tri-*n*-octylamine in an organic solvent and subsequently re-extracted into an aqueous phase. The results compare well with those attained by using methods given in the Czechoslovak State Standard and in the standard of the Czechoslovak Uranium Industry corporation.

Environmental protection demands associated with the mining and processing of uranium ores call for more and more sensitive and accurate methods for the determination of uranium in surface waters and waste waters. Spectrophotometric and extraction photometric methods are routine in conventionally equipped laboratories. A survey of spectrophotometric methods of uranium determination can be found, e.g., in refs<sup>1-5</sup>. From among organic dyes, Arsenazo III, 2-(5-bromo-2-pyridylazo)-5-(diethylamino)phenol (5-Br-PADAP) and some triphenylmethane dyes, particularly in the presence of surfactants, are the most important in this respect.

The aim of the present work was to compare spectrophotometric methods for the determination of uranium(VI) with eriochromazurol B (refs<sup>4,6,7</sup>), chromazurol S (ref.<sup>7</sup>) eriochromcyanine R (ref.<sup>8</sup>), 5-Br-PADAP<sup>9</sup>, the method<sup>10</sup> and its modification<sup>11</sup>, and the method according to Czechoslovak State Standard 83 0533 (ref.<sup>12</sup>), with regard to their sensitivity, accuracy, repeatability, time demand and tediousness.

### EXPERIMENTAL

#### Chemicals and Solutions

A standard solution of uranium in 0.2M-HCl ( $c_U = 0.189 \text{ mol l}^{-1}$ ) was prepared from  $\text{UO}_2\text{Cl}_2 \cdot 2 \text{H}_2\text{O}$  of analytical purity (Lachema, Brno) and standardized gravimetrically via 8-hydroxyquinolate. Alternatively used was a solution of uranyl chloride at a concentration of  $c_U = 4.2 \text{ mmol l}^{-1}$  (1.000 g U/l), prepared by dissolving 1.000 g of uranium metal (shavings of

uranium of nuclear grade purity) in 10 ml of concentrated hydrochloric acid containing several drops of 30%  $\text{H}_2\text{O}_2$ , transferring the solution into a 1 000 ml volumetric flask, adding 42 ml of concentrated HCl and diluting to the mark with redistilled water.

Dilute uranium solutions ( $c_U < 10 \mu\text{mol l}^{-1}$ ) are unstable unless uranium is bonded in stable complexes<sup>13-17</sup>; this also applies to relatively strongly acid solutions. The cause of this is an easy hydrolysis of uranyl solutions and, in particular, sorption of uranium on the surface of vessels in which it is stored; this sorption is most pronounced on glass and is lower on polyethylene and still lower on teflon<sup>13</sup>. As a result of these phenomena, the free concentration of uranium in the sample stored decreases with time. With regard to this, dilute working solutions of uranium were used for several days only, and the given waste water sample (as well as the model sample) was analyzed by all the methods in the same time period from the sampling.

Eriochromazuröl B (CAB),  $\text{C}_{23}\text{H}_{16}\text{Cl}_2\text{O}_6$ , was obtained by repeated precipitation of an alkaline solution of the disodium salt (Carlo Erba, Italy) after acidification to pH 2.2 (2M-HCl); the precipitate was repeatedly rinsed with 0.01M-HCl. The preparation was dried in a desiccator over solid KOH and equilibrated in air to constant weight, and the active content was checked by elemental analysis (C, H). The chemical contained about 98% active component with respect to the anhydrous preparation.

Chromazuröl S (CAS),  $\text{C}_{23}\text{H}_{16}\text{Cl}_2\text{O}_9 \cdot 2 \text{H}_2\text{O}$ , was prepared from the trisodium salt (Geigy, Basel) after conversion to the free acid and purifying from CAB by a combination of the precipitation and extraction procedures<sup>18,19</sup>. The active content, as established by C, H elemental analysis, was 89% with respect to the dihydrate.

Eriochromocyanine R (ECR),  $\text{C}_{23}\text{H}_{18}\text{O}_9 \cdot 2 \text{H}_2\text{O}$ , was obtained from an aqueous solution of the trisodium salt (Lachema, Brno) by precipitation with 2M-HCl. The precipitate was filtered out, rinsed with 2M-HCl and water, dried in a desiccator over solid KOH, and equilibrated in air to constant weight.

The purity of the reagents was checked chromatographically on Silufol Extra Pure (20 cm  $\times$  20 cm) foils, pre-activated for 30 min at 110°C and deactivated for 4 h in air at room temperature. The chromatograms were developed in DESAG chromatographic cuvettes after saturating the compartment with vapours in the butanol-acetic acid-water 7 : 1 : 5 system.

Stock solutions of the triphenylmethane (TPM) dyes were prepared so that the chemicals were dissolved in a small volume of 5M ammonia, diluted with redistilled water, adjusted with HCl to pH 9, and diluted to volume with redistilled water.

5-Br-PADAP (5BP),  $\text{C}_{15}\text{H}_{17}\text{BrN}_4\text{O}$  (Merck, Darmstadt), was used in solution at a concentration of 0.1 mmol  $\text{l}^{-1}$  in 99.5% dimethylformamide.

Arsenazo III (AA),  $\text{C}_{22}\text{H}_{18}\text{As}_2\text{N}_4\text{O}_{14}\text{S}_2$ , reagent of grade purity (Lachema, Brno); a high-purity, chromatographically purified preparation of this reagent<sup>20</sup> (AAR), was also employed. Working solution of arsenazo III for the PNU method<sup>10</sup> and its modification<sup>11</sup> was prepared by dissolving 280 mg of the chemical and 50 g of oxalic acid (dihydrate) in 80 ml of fluoroboric acid (40%), adding 80 ml of concentrated HCl, and diluting to 1 000 ml with ethanol. For the method according to the Czechoslovak State Standard<sup>12</sup>, 2.5 g of AA was dissolved in a 0.02M-NaOH solution and diluted with this solution to 1 000 ml.

Septonex (SPX),  $\text{C}_{21}\text{H}_{44}\text{BrNO}$  (Slovakofarma, Hlohovec), was purified by dissolving it in 20–50 ml of hot ethanol, filtering the solution, and precipitating dropwise with diethyl ether. The surfactant separated was filtered out and dried in a desiccator in a vacuum by using  $\text{CaCl}_2$ .

† Cetylpyridinium bromide (CPB),  $\text{C}_{21}\text{H}_{38}\text{BrN}$  (Lachema, Brno), was purified by the same procedure as Septonex. Stock solutions of the cationic surfactants were obtained by dissolving the chemicals in ethanol.

Triton X-100 (TNX), octylphenolpolyethylene glycol ether, (Koch-Light, U.K.), was used

as a 2% stock solution in redistilled water; tri-*n*-octylamine (TOA), C<sub>24</sub>H<sub>51</sub>N (Merck-Schuchardt, F.R.G.), was used as a 0.1M solution in benzene (freon).

Tributyl phosphate (TBF) (BDH, U.K.); the extraction mixture was prepared by mixing one volume of TBF with two volumes of benzene (freon).

Benzene (B) of p.p. purity (Lachema, Brno); kerosene (K), b.p. 130–280°C (Slovnaft, Bratislava); Freon 113 (F) (Du Pont, Geneva).

Denaturated ethanol (EtOH) was distilled on a column in the presence of EDTA. The main distillate fraction contained 4.3–4.4% water and 3.9–4.2% methanol.

Pyridine buffer (PYR) (2 mol l<sup>-1</sup>) was prepared by diluting pyridine (Zaklady koksochemiczne, Chorzow) with redistilled water and titrating to pH 6.0 or 5.6 with isothermal HCl<sup>7,8</sup> or HNO<sub>3</sub><sup>4,6</sup> (pH 5.0), followed by dilution to 100 ml with redistilled water.

Triethanol buffer (TEA) (1 mol l<sup>-1</sup>) was prepared from a chemical of reagent grade purity (Merck, Darmstadt) by dissolving it in water, adjusting to pH 7.0 with H<sub>2</sub>SO<sub>4</sub>, and diluting in a volumetric flask to the mark<sup>7</sup>. For the 5BP method<sup>9</sup>, the pH was adjusted to 8.3 with HClO<sub>4</sub> of reagent grade purity, and the solution was diluted to 100 ml with redistilled water.

Isothermal acids and ammonia were prepared from commercial analytical grade chemicals by isothermal distillation in a dessicator. Redistilled water was obtained in an all-quartz distillator (Heraeus); it was used throughout the work. Masking mixtures and other requisite chemicals are described in detail in the respective papers which the reader has been referred to.

#### Model Uranium Sample

The composition of the model uranium sample is given in Table I.

#### Apparatus

A PHM-64 pH-meter (Radiometer, Copenhagen) equipped with a G202B glass electrode and a K401 calomel electrode. A Super Scan 3 recording double-beam UV-VIS spectrophotometer (Varian-Techtron, Australia); a SPEKOL spectrophotometer (Carl Zeiss, Jena); 1 cm cells.

#### Data Handling

The program STAT<sup>21</sup> was employed for calculating the parameters of the calibration curves ( $A = \epsilon c + A_0$ ); recommended relations and methods<sup>21,22</sup> were used for other data handling. Sensitivity was expressed in terms of Sandell's index (in  $\mu\text{g ml}^{-1}$ ):

$$SI(A = 0.010) = 10M/\epsilon, \quad (1)$$

and the limit of determination was expressed as<sup>23</sup>

$$A_{\text{lim}} = \langle A \rangle_0 + 10 s_0 \quad (2)$$

$$c_{\text{lim}} = 10^4 s_0 M / \epsilon \quad (\mu\text{g ml}^{-1}), \quad (3)$$

where  $s_0$  is the standard deviation estimate of the blank,  $\langle A \rangle_0$  is the arithmetic mean of the observed blank absorbances ( $n = 10$ ), and  $M$  is the molar mass of uranium.

The  $T_{s,n}$  or  $T_{s,1}$  criterion (Grubbs' test) at  $\alpha = 0.05$  was used for elimination of outliers<sup>22</sup>.

#### Principles of the Methods for the Determination of Uranium

A survey of the characteristics of the spectrophotometric and extraction photometric methods

for the determination of uranium is given in Table II. Sample handling for all the methods was done according to ref.<sup>10</sup>.

#### Determination of Dissolved Uranium

An aliquot of water analyzed is evaporated to dryness in a porcelain dish with 0.5 ml of concentrated HCl per 25 ml of sample and with 2 ml of 30% H<sub>2</sub>O<sub>2</sub>. The evaporation residue is handled specifically by the various methods.

#### Determination of Undissolved Uranium

A membrane filter (0.45 μm) with the trapped insolubles<sup>10</sup> is transferred into a teflon beaker or a platinum dish, and 5 ml of redistilled water, 2 ml of concentrated nitric acid and 0.5 ml of sulfuric acid (1 : 1) are added. After dissolution of the filter, 2 ml of concentrated hydrofluoric acid are added and the whole is evaporated until white fumes appear; 1 ml of HF is then added and the mixture is evaporated to dryness. The residue is wetted with 5 ml of 6M-HCl, heated gently and transferred into a 250 ml volumetric flask. Redistilled water is added to the mark and the solution is filtered through a dry filter. Further procedure as in the determination of dissolved uranium.

Details concerning the analytical methods can be found in refs<sup>4,6-12</sup>.

TABLE I

Composition of model uranium sample

X <sup>a</sup>	$\rho_X$ μg l <sup>-1</sup>	$c_X$ μmol l <sup>-1</sup>	$u_X = \rho_X/\rho_{U(VI)}$	$p_X = c_X/c_{U(VI)}$
U(VI)	250	1.05	1.0	1.00
Th(IV)	50	0.215	0.2	0.20
Zr(IV)	50	0.548	0.2	0.52
Ti(IV)	50	1.04	0.2	0.99
Fe <sup>3+</sup>	10 000	179	40.0	170.48
Cr <sup>3+</sup>	50	0.962	0.2	0.92
Al <sup>3+</sup>	500	18.5	2.0	17.62
Cu <sup>2+</sup>	50	0.787	0.2	0.75
Ni <sup>2+</sup>	50	0.852	0.2	0.81
Mn <sup>2+</sup>	50	0.910	0.2	0.87
Be <sup>2+</sup>	50	5.55	0.2	5.29
Cl <sup>-</sup>	35 000	987	140.0	940.00
SO <sub>4</sub> <sup>2-</sup>	2 000 000	20 800	8 000.0	19 809.52
NO <sub>3</sub> <sup>-</sup>	50 000	806	200.0	767.62
Citric acid	10 000	52.1	40.0	49.62
Humic acids	1 700 <sup>b</sup>	—	—	—

<sup>a</sup> Anions in the H<sup>+</sup> or Na<sup>+</sup> form, solution pH 2.58; <sup>b</sup> content corresponding to COD.

## RESULTS AND DISCUSSION

The following criteria are most significant in comparing the various analytical methods: sensitivity, accuracy, repeatability, tediousness and time and economic demands.

*Method Sensitivity*

Sensitivity of the methods (molar absorptivity values) and their limits of determination can be assessed from the calibration curves. The results are given in Table III.

TABLE II

Characteristics of the spectrophotometric and extraction photometric methods for the determination of uranium

Method	Uranium separation			Colouration			
	<i>a</i>	<i>b</i>	<i>c</i>	Dye	Surfactant	Medium, buffer	pH
CAS-B	4M-HCl	TOA in benzene	0.3M-HCl	CAS	SPX	Cl <sup>-</sup> , pyridine	6.0
CAS-K	4M-HCl	TOA in kerosene	0.3M-HCl	CAS	SPX	Cl <sup>-</sup> , pyridine	6.0
CAB	4M-HCl	TOA in benzene	0.3M-HCl	CAB	SPX	Cl <sup>-</sup> , pyridine	5.6
ECR	4M-HCl	TOA in benzene	0.3M-HCl	ECR	SPX	Cl <sup>-</sup> , pyridine	5.6
CAS-F	4M-HCl	TOA in freon	0.3M-HCl	CAS	SPX	SO <sub>4</sub> <sup>2-</sup> , TEA	7.0
CPB	4M-HCl	TOA in benzene	0.3M-HCl	CAB	CPB	NO <sub>3</sub> <sup>-</sup> , pyridine	5.0
5BP	4M-HCl	TOA in benzene	0.3M-HCl	5BP	TNX	ClO <sub>4</sub> <sup>-</sup> , TEA, DMF	7.3
PNU	6M-HCl	TBF in benzene	—	AAR	—	TBF, benzene	H <sup>+</sup>
PNU-AA				AA		EtOH, water	
PNU-F	6M-HCl	TBF in freon	—	AAR	—	TBF, freon EtOH, water	H <sup>+</sup>
CSS-AA <sup>d</sup>	sorption on silica gel, washing with washing solution and water, elution with 3M-acetic acid			AA	—	CH <sub>3</sub> COOH	H <sup>+</sup>

<sup>a</sup> Extraction from; <sup>b</sup> extractant; <sup>c</sup> reextractant; <sup>d</sup> Czechoslovak State Standard.

The method based on the use of chromazurol S in the presence of Septonex (CAS-B) is the most sensitive. Also, the limits of determination attained in the methods of uranium determination with triphenylmethane dyes in the presence of surfactant are considerably lower than in the methods using arsenazo III. The sensitivity and limit of determination in the 5BP method are at the level of the PNU method. The higher limit of determination in the PNU method as compared to the methods with TPM dyes may be due to the slight turbidity of the solutions measured.

#### *Accuracy and Repeatability of the Methods*

*Model uranium sample.* The accuracy of the methods was compared on the results of analyses of the model uranium sample. Each determination was performed in 10 parallel experiments. The results are summarized in Table IV. The most accurate results emerged from the analysis by the CAS-B method (+1.2 rel. %). The other methods based on the use of triphenylmethane dyes also gave good results, which were 1.9 rel. % higher than the true value.

From the repeatability point of view, the methods can be arranged in the following order (based on experiments with the model uranium sample): methods based on the use of triphenylmethane dyes in the presence of SPX and the 5BP method, the CAS-B method again giving the best results ( $s_r = 1.2$  rel. %); the CPB method and the methods using arsenazo III, i.e. the PNU method and the Czechoslovak State

TABLE III

Comparison of methods for the determination of uranium from the sensitivity point of view

Method	$\varepsilon \mp s(\varepsilon)$ $l \text{ mol}^{-1} \text{ cm}^{-1}$	$SI$ $\mu\text{g ml}^{-1}$	$Q_{\text{lim}}$ $\mu\text{g ml}^{-1}$
CAS-B	147 290 $\mp$ 1 430 <sup>a</sup>	0.016	0.036
CAS-K	140 530 $\mp$ 660 <sup>a</sup>	0.017	0.037
CAB	140 440 $\mp$ 650 <sup>a</sup>	0.017	0.047
ECR	91 110 $\mp$ 700 <sup>b</sup>	0.026	0.063
CAS-F	117 955 $\mp$ 2 610 <sup>b</sup>	0.022	0.012
CPB	111 270 $\mp$ 930 <sup>a</sup>	0.023	0.050
5BP	69 800 $\mp$ 790 <sup>c</sup>	0.031	0.128
PNU	68 700 $\mp$ 1 220 <sup>b</sup>	0.035	0.107
PNU-AA	37 310 $\mp$ 570 <sup>a</sup>	0.067	0.197
PNU-F	66 650 $\mp$ 2 600 <sup>b</sup>	0.037	0.073
CSS-AA	29 920 $\mp$ 600 <sup>a</sup>	0.083	0.258

Uranium concentration region ( $\mu\text{mol l}^{-1}$ ): <sup>a</sup> 0.84–6.3; <sup>b</sup> 0.5–10; <sup>c</sup> 0.19–14.

Standard-AA method, provided somewhat poorer results ( $s_r = 2.5, 3.3$  and  $3.5\%$ , respectively).

The higher results emerging when using the PNU method can be explained in terms of the occurrence of a turbidity in the solutions measured; this, however, was not observed when freon was employed<sup>11</sup>. The lower results and poorer repeatability in the Czechoslovak State Standard-AA method may be due either to a lower sensitivity of the method or to different processes associated with the sorption and elution at different uranium concentrations.

*Surface water and waste water samples.* The results of determination of uranium in surface waters and waste waters by the various methods are given in Tables V and VI. The tables demonstrate that well comparable analytical results from the various methods were obtained for HA2, HA2-n and PR1 samples, where the differences between the lowest and highest concentrations were 1.9, 3.2 and 5.6 rel. %, respectively. The differences were higher for the samples HA1 and DR1 (11.8 and 14.1 rel. %, respectively); this was due to the CPB method giving exceedingly low results. If these results are omitted, the differences between the lowest and highest result are at a level approaching that for the PR1 sample, viz. 5.9 and 8.3 rel. %. The average difference between the lowest and highest uranium concentrations in all practical samples is 7.3 rel. %, and if the results obtained by the CPB method for

TABLE IV

Comparison of accuracy and repeatability of methods for the determination of uranium on a model sample (MS)

Method	$\langle x \rangle \pm s^a$ $\mu\text{g U/l}$	$e^b$ %	$s_r$ %
CAS-B	253.0 $\pm$ 3.0	1.2	1.2
CAS-K	255.0 $\pm$ 5.1	2.0	2.0
CAB	253.6 $\pm$ 4.3	1.4	1.7
ECR	255.5 $\pm$ 5.9	2.2	2.3
CAS-F	244.8 $\pm$ 3.2	2.1	1.3
CPB	253.4 $\pm$ 6.3	1.4	2.5
SBP	244.6 $\pm$ 4.6	2.2	1.9
PNU	265.5 $\pm$ 5.6	6.2	2.1
PNU-AA	270.6 $\pm$ 12.2	8.2	4.5
PNU-F	243.8 $\pm$ 8.0	2.5	3.3
CSS-AA	236.2 $\pm$ 8.3	5.5	3.5

<sup>a</sup> True uranium concentration 250  $\mu\text{g/l}$ , 10 parallel determinations; <sup>b</sup> relative error.

the HA1 and DR1 samples are omitted, the average difference decreases to mere 5.0 rel. %. In view of the fact that the highest permitted difference between two parallel determinations by the method according to the PNU standard must not exceed 12 rel. % for 10–50 µg U/l, 6 rel. % for 50–100 µg U/l, 5 rel. % for 100 to

TABLE V

Comparison of methods for the determination of uranium on surface water and waste water samples PR1 and DR1

Method	$\langle x \rangle \mp s, \mu\text{g U/l}$	
	PR1 <sup>a</sup>	DR1 <sup>a</sup>
CAS-B	35.3 $\mp$ 0.9	312.1 $\mp$ 5.3
CAB	35.1 $\mp$ 1.8	—
ECR	35.9 $\mp$ 1.3	304.9 $\mp$ 7.3
CAS-F	36.2 $\mp$ 1.2	308.2 $\mp$ 5.5
CPB	35.8 $\mp$ 1.6	278.0 $\mp$ 8.1
5BP	—	304.7 $\mp$ 9.7
PNU	35.3 $\mp$ 1.0	323.9 $\mp$ 8.4
PNU-F	37.2 $\mp$ 1.1	315.8 $\mp$ 8.5
CSS-AA	35.6 $\mp$ 1.2	317.6 $\mp$ 9.2

<sup>a</sup> Calculated always from 5 parallel determinations.

TABLE VI

Comparison of methods for the determination of uranium on surface water and waste water samples HA1 and HA2

Method	$\langle x \rangle \pm s, \mu\text{g U/l}$		
	HA1 <sup>b</sup>	HA2 <sup>b</sup>	HA2-n <sup>a,b</sup>
CAS-B	105.5 $\mp$ 1.8	285.0 $\mp$ 4.6	254.6 $\mp$ 2.8
CAB	103.5 $\mp$ 2.2	286.8 $\mp$ 7.5	250.8 $\mp$ 4.0
CPB	97.4 $\mp$ 1.5	287.8 $\mp$ 7.5	251.0 $\mp$ 2.8
5BP	101.2 $\mp$ 2.0	—	—
PNU	110.5 $\mp$ 1.9	285.6 $\mp$ 6.6	259.1 $\mp$ 7.5
CSS-AA	102.3 $\mp$ 4.2	282.2 $\mp$ 16.1	258.6 $\mp$ 13.4

<sup>a</sup> Undissolved uranium forms; <sup>b</sup> calculated always from 5 parallel determinations.

300  $\mu\text{g U/l}$  and 4 rel. % for more than 300  $\mu\text{g U/l}$  (ref.<sup>10</sup>) and the difference obtained by us for all the methods tested was 5.0 rel. %, our determination can be considered rather precise. And since the methods compared are in a sense independent (Czechoslovak State Standard, PNU, triphenylmethane dyes), it is reasonable to assume that this relatively high precision also implies relative high accuracy.

The lower results by the CPB method for some samples may be due to time instability of the samples: the complexes probably decompose in the presence of some substances, e.g. humic acids. The higher results afforded for some samples by the PNU method, on the other hand, may be due to a slight haze of the solutions or to the presence of interfering ions such as those of Th, Zr or rare earth elements. (For details concerning the interfering effects in the various methods see the references.)

A survey of repeatabilities of the various methods is given in Table VII. The relative standard deviations for the surface water and waste water samples document that all of the methods except the Czechoslovak State Standard method are very well repeatable (2.5 rel. % on average). The best repeatability was achieved with the CAS-B method (1.8 rel. %), and only the Czechoslovak State Standard-AA method exhibited a poorer repeatability (4.2 rel. %), which – as mentioned above – can be due to its lower sensitivity or to various processes during the sorption and elution of different uranium concentrations.

TABLE VII  
Comparison of methods for the determination of uranium from the repeatability point of view

Method	$s_r$ , %, for sample						$\langle s_r \rangle$ , %	
	MS	PR1	DR1	HA1	HA2	HA2-n	<i>a</i>	<i>b</i>
CAS-B	1.2	2.6	1.7	1.7	1.6	1.1	1.8	1.7
CAS-K	2.0	—	—	—	—	—	—	2.0
CAB	1.7	5.1	—	2.1	2.6	1.6	2.9	2.6
ECR	2.3	3.7	2.4	—	—	—	3.0	2.8
CAS-F	1.3	3.2	1.8	—	—	—	2.5	2.1
CPB	2.5	4.5	2.9	1.6	2.6	1.1	2.5	2.5
5BP	1.9	—	3.2	2.0	—	—	2.6	2.4
PNU	2.1	2.7	2.6	1.7	2.3	2.9	2.5	2.4
PNU-AA	4.5	—	—	—	—	—	—	4.5
PNU-F	3.3	2.9	2.7	—	—	—	2.8	2.9
CSS-AA	3.5	3.3	2.9	4.1	5.7	5.2	4.2	4.1

Average  $s_r$  value for the determination of uranium in <sup>a</sup> surface water and waste water samples; <sup>b</sup> all samples analyzed.

*Tediousness and Time and Economic Demands*

Tediousness and time consumption also constitute an important criterion for assessing the various methods. The basic procedures of the methods, along with the time consumption by an analysis, are summarized in Table VIII.

The most favourable from this point of view is the PNU method (as well as its freon variant), because it includes mere four operations and an analysis takes 10 min only. Thus it suits best to automation for routine analyses. The methods using TPM dyes and the 5BP method are comparably tedious and time consuming (8 operations, 15–25 min). The most tedious and time consuming is the Czechoslovak State Standard-AA method, which involves 9 operations and takes approximately 240 min, although in routine operation its time consumption is decreasing. As to the economic demands (chemicals, instrumentation), the methods are basically comparable.

TABLE VIII

Comparison of the methods from the tediousness and time consumption points of view

Method	Basic operations	Number of operations	Time of an analysis min
CAS-B CAS-K CAB ECR	Evaporation residue leaching, Fe(III) reduction, extraction, washing, double reextraction, colouration (4 components), measurement	8	15–25
CAS-F	Evaporation residue leaching, Fe(III) reduction, double extraction, reextraction, pipetting, colouration (5 components), measurement	8	20
CPB	colouration (5 components), otherwise as in the CAS-B method	8	25
5BP	colouration (6 components), otherwise as in the CAS-B method	8	20
PNU PNU-AA	Evaporation residue leaching, extraction, colouration (1 component), measurement	4	10
PNU-F	Colouration (2 components), otherwise as with the PNU method	4	10
CSS-AA	Column regeneration, evaporation residue leaching, pH adjustment, sorption, double washing, elution, colouration (6 components), measurement	9	240

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