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## MULTI-ELEMENTAL INDUCTIVELY COUPLED PLASMA-OPTICAL EMISSION SPECTROSCOPIC CALIBRATION PROBLEMS OF THE SEQUENTIAL EXTRACTION PROCEDURE FOR THE FRACTIONATION OF THE HEAVY METAL CONTENT FROM AQUATIC SEDIMENTS

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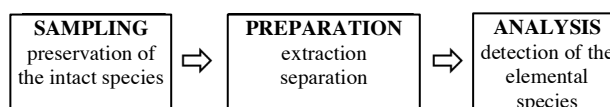
For the characterisation of the environmental mobility of heavy metal contamination in aquatic sediments, the EU Bureau of Reference has proposed a fractionation by sequential extraction procedure. For its validation, the CRM-701 sample is available containing Cd, Cr, Cu, Ni, Pb, and Zn. In this paper, the matrix-matched calibration problems are presented. A multi-elemental inductively coupled plasma-optical emission technique is employed for the detection of heavy metals in the extracts. It was established that the sensitivities are strongly influenced by the extractants, which causes significant matrix effects: the sensitivities are strongly influenced by the solvents applied in extraction steps; the summarised recoveries show an acceptable agreement with the certified values; however, in the individual extraction steps for certain elements significant differences may occur due to the neglected interferences. Therefore, further optimisation is required utilising the flexible line selection possibility offered by the HORIBA Jobin Yvon ACTIVA-M instrument.

**Keywords:** fractionation, sequential extraction, multi-elemental ICP-OES, matrix-matched calibration, heavy metal contamination, sediments

### 1. Introduction

Environmentally toxic elements, such as heavy metals, are the most significant inorganic pollutants. The role of different chemical elements in food production has been an important question of agrochemical research since the middle of the nineteenth century. Numerous extraction methods have been developed for determining biologically available fractions of nutritionally relevant elements in soils. Environmental researchers have confronted similar problems over the last few decades of the twentieth century in characterising the human- and eco-toxicological impacts of increasing heavy metal pollution. This challenge has created new requirements for analytical methodology and contributed to the development of speciation analytical chemistry. This scientific discipline provides the foundation for the evaluation of toxicological impacts of chemical elemental species detectable in environmental systems [1,2]. In such procedures, the original physico-chemical structural forms of chemical elements present in the system must be preserved during sampling and sample preparation. Then, appropriate separation methods must be applied before element specific analytical detection (*Fig.1*).

The European Union established the European Virtual Institute for Speciation Analysis in 2002 for promoting cooperation, collection, reviewing, and discussion of information and knowledge related to chemical speciation analysis ([www.speciation.net](http://www.speciation.net)). Attention was drawn to the mobility and biological impact of heavy metals in environmental systems influenced by their chemical speciation. Biological risk assessment of contaminated areas therefore requires the total speciation of all chemical elements present in the system. However, due to the complex structure of solid environmental samples (e.g. soils, sediments, gravitation dust, mining waste, etc.), these analytical tasks in practice cannot be fully completed. As a compromise, the fractionation of the heavy metal content according to environmental mobility and estimation of biological availability by sequential extraction procedures have become the main research approaches. Papers published in this area and their citations exponentially increased in the period of 1995



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Figure 1. Scheme of the speciation analysis procedure.

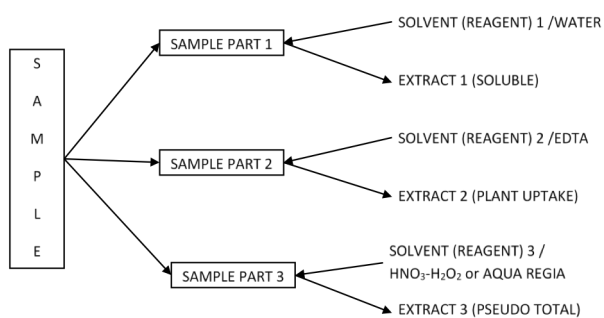


Figure 2. Strategy of serial single-step extractions.

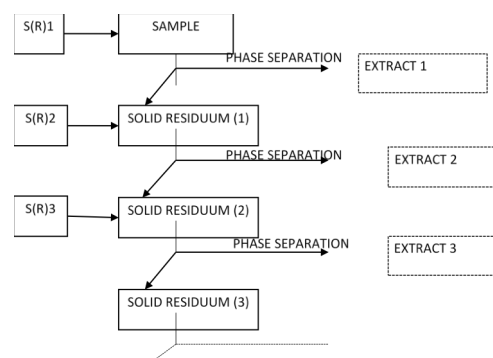
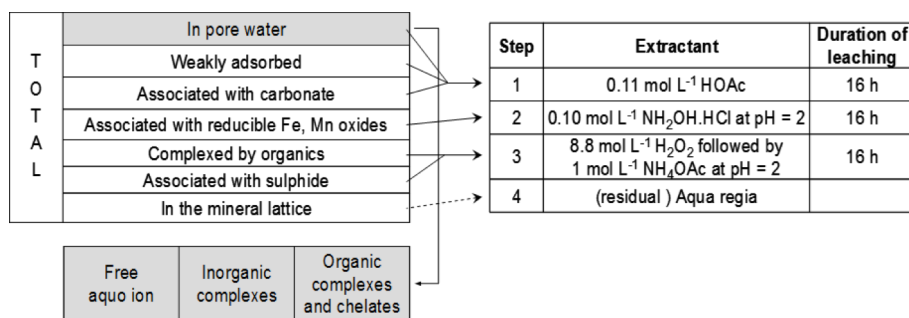


Figure 3. Strategy of sequential extractions (S(R) stands for SOLVENT(REAGENT)).



Scheme 1. Element fractions in aquatic sediment as classified by Kersten and Förstner [4], Caroli [3], and Tessier [5] (left-hand side) and the original BCR sequential extraction steps [6-8] (right-hand side)

and 2013: from 200/year to 700/year; according to related citations from 1000/year to 19,000/year based on Thomson Reuters, Web of Science database. A primary risk assessment of heavy metal contamination in the soil/water/atmosphere system was based on the fractionation of metallic element content of environmental samples according to their environmental mobility. The term “fractionation” was recommended by the IUPAC in 2000 [2]. The mobility of an element according to the different solubilities of different binding classes can be estimated by solvents sequentially applied containing physico-chemically increasingly aggressive reagents [3,4]. In agricultural chemistry, the serial single step strategy (Fig.2), in environmental chemistry the strategy of sequential extraction has become dominant (Fig.3).

The first sequential extraction procedure for the characterisation of the mobility of heavy metals in aquatic sediments was developed by Tessier *et al.* [5], who classified the metal content of sediments according to the solubility and binding forms of metallic species as presented in Scheme 1.

Based on this essential work [5], numerous 5-8-step sequential extraction schemes have been developed by which the original chemical structures (binding forms) are gradually dissolved and/or decomposed [9]. The complete duration of these procedures is 5–6 days, while the duration of the batch leaching steps is determined by a long setup time of solubility and heterogeneous chemical equilibria. The proposal for a 3(+1)-step sequential extraction procedure issued by BCR in 1993 is a simplified version of the above-mentioned schemes [6], but it is still time-consuming and labour-intensive.

As shown in Scheme 1, the water soluble, weakly adsorbed, and carbonate-associated metal fractions are extracted simultaneously by acetic acid in the first leaching step. In the second step, the metal fractions associated with reducible Fe and Mn oxides are produced after reduction by hydroxylamine. A fraction of metals coordinated to organic molecules and associated with sulphides is extracted after oxidation by H<sub>2</sub>O<sub>2</sub> in the third step. In the extra step, the residual fraction can be obtained by means of digestion with *aqua regia* or HNO<sub>3</sub>/H<sub>2</sub>O<sub>2</sub>.

Re-adsorption of extracted metals during phase separation can lead to analyte losses. In the extracts, the high concentration of the reagent may cause strong matrix effects during spectrochemical element detection. The CRM 601 sediment reference material issued in 1997 has been certified for this procedure only for Cd, Cr, Ni, Pb, and Zn [7,8]. During the analysis of the BCR 701 sediment materials, the original BCR procedure was modified to avoid analyte loss during the second leaching step due to pH instability [10–13]. However, this modification in BCR procedure may cause significant differences relative to previously obtained data. The BCR procedures in their original and modified versions were successfully applied to aquatic sediments and soils; however, soil CRM has not been issued for this procedure up to now [14–21].

It can be concluded that the Tessier-based fractionation procedures [5] are widely used for heavy metal contamination assessments in soils and aquatic sediments, but the realistic interpretation of these data requires standardisation. However, this has been hindered due to methodological problems of measurements and analysis [22–23]. These problems limiting the application of the BCR sequential

*Table 1.* Overview of the cooperative research projects between Szent István University Gödöllő and the Technical University Košice

Limitations of the BCR scheme	Achievements by SZIE and TU Košice research groups
Does not match the natural mobilisation pathways	→ Better modelling of environmental mobility by the application of H <sub>2</sub> O and H <sub>2</sub> O/CO <sub>2</sub> solvents [24].
Does not preserve the intact species of the sample	→ Application of aqueous extractions for the elaboration of biological tests [25].
Time consuming (4-5 days)	→ Acceleration of batch leaching by means of sonification [26]. → Development of continuous flow operation in the supercritical fluid extractor for CO <sub>2</sub> , H <sub>2</sub> O and H <sub>2</sub> O/CO <sub>2</sub> solvents [24]
Cross-contamination during operation and applied reagent	→ Reduction of operations and reagents
Limited applicability and validation:	
Validation and available CRM only for sediments	→ Extension of the application to other matrices: soils, gravitation dusts, biofilms, red mud, and composts [26-30].
Validation of the procedure for Cd, Cr, Cu, Ni, Pb, Zn	→ Multi-elemental calibration and validation for different matrices and extracts [27].
High reagent and organic content of the extracts	

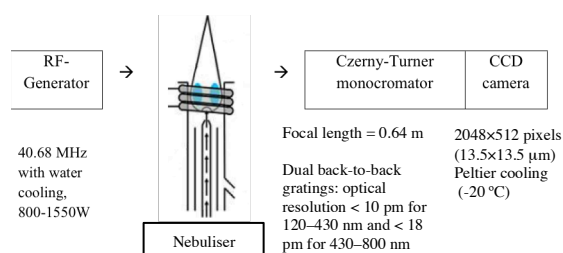
extraction procedure have initiated a cooperative research project between Szent István University Gödöllő and the Technical University Košice as summarised in *Table 1*.

The aim of the given study was the evaluation of changes in the environmental mobility of heavy metals at two polluted areas (Upper Tisza/2000–2001 and Gödöllő-Isaszeg lake system/1995–1998) by means of the repeated BCR fractionation of heavy metals in the sediments and soils [31–34]. A flexible, multi-elemental Inductively Coupled Plasma-Optical Emission (ICP-OES) technique with a Charge-Coupled Device (CCD)-detection system was employed instead of the formerly applied flame atomic absorption spectroscopy (FAAS). The latter had to be optimised for each analyte element individually. Hereby, the problems of the matrix-matched multi-elemental calibration of the ICP-OES method are described using different solvent applied from the BCR procedure. The validation of the calibration was controlled by the fractionation of the CRM 701 sample.

## 2. Experimental

### 2.1. Elemental Analysis and Instrumentation

For element detection in different extractant matrices, the HORIBA Jobin Yvon ACTIVA-M ICP-OES spectrometer was employed, which is able to record the entire UV-vis spectrum range by rapid scanning CCD-detection. It also makes possible the flexible analytical line selection for 75 elements. The wavelength scale calibration of recorded spectra is based on a reference line position set by the user. The C 193.026 nm line is proposed by the manufacturer in routine analytical applications. The instrument's scheme and technical



*Figure 4.* Scheme of the HORIBA Jobin Yvon ACTIVA-M ICP-OES spectrometer and relevant technical parameters

parameters are presented in *Fig.4*. Introduction of the sample can be performed by a concentric glass nebuliser and glass cyclone spray chamber fed by a 3-channel peristaltic pump.

### 2.2. ICP-OES Operation Parameters

The operation parameters of ICP-OES were selected on the basis of the manufacturer's manual proposed for multi-elemental analysis as follows:

- Incident power: 1000 W,
- Plasma gas flow: 13.14 dm<sup>3</sup> min<sup>-1</sup>,
- Sheath gas flow: 0.32 dm<sup>3</sup> min<sup>-1</sup>,
- Nebuliser gas flow: 0.28 dm<sup>3</sup> min<sup>-1</sup>,
- Nebuliser gas pressure: 2.86 bar, and
- Nebuliser sample flow uptake: 0.85 cm<sup>3</sup> min<sup>-1</sup>.

### 2.3. Matrix Matched Calibration Solutions

Amounts of 1 mg dm<sup>-3</sup> (in cc HNO<sub>3</sub>) mono-elemental Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, V, and Zn (Précis Certified Standards for ICP Spectroscopy, HORIBA Scientific, France) standard solutions corresponding to 0, 5, and 20 mg dm<sup>-3</sup> concentrations were pipetted into a 50 cm<sup>3</sup> volumetric flask and then diluted by solvents applied in the BCR sequential extraction procedure:

- 1<sup>st</sup> step: 0.11 M acetic acid.
- 2<sup>nd</sup> step: 0.1 M hydroxylamine-hydrochloride.
- 3<sup>rd</sup> step: 1 M ammonium acetate.
- extra step: 13 g/g nitric acid.

### 2.4. Analytical Lines

The following analytical lines were selected according to the manufacturer's proposal for multi-elemental analysis:

- Cd 214.441 nm
- Co 230.785 nm
- Cr 205.571 nm
- Cu 324.754 nm
- Fe 259.940 nm and 240.489 nm
- Mn 257.610 nm
- Ni 222.296 nm (instead of 221.650 nm!)
- Pb 220.353 nm
- V 309.311 nm
- Zn 213.857 nm

In the first, second, and extra step, the wavelength readout started from the C 193.026 nm reference line. In the third step, the correct wavelength readout was only

*Table 2.* The calibration lines ( $y = mx+b$ , at wave length  $\lambda$  in nm), correlation  $R^2$  values, residual standard deviations (RSD), background equivalent concentrations (BEC in  $\mu\text{g dm}^{-3}$ ), and detection limits ( $C_{L(3\sigma)}$  in  $\mu\text{g dm}^{-3}$ ) obtained by a 0.11 M acetic acid matrix.

	$\lambda$	$C_{L(3\sigma)}$	BEC	$m$	$b$	$R^2$	RSD
Cd	214.441	0.5	65	43778	2867	0.9999	1.1%
Co	230.785	0.8	145	41860	6064.7	0.9997	2.5%
Cr	205.571	1.5	174	18298	3184.2	0.9996	2.9%
Cu	324.754	0.2	121	159951	19374	0.9998	2.0%
Fe	259.940	0.5	72	205720	14716	0.9999	1.2%
Mn	257.610	0.2	105	902188	94673	0.9999	1.8%
Ni	222.296	2.0	115	7154	823.38	0.9998	2.0%
Pb	220.353	3.5	17	4087.4	68.946	1.0000	0.3%
V	309.311	0.6	34	259817	8897	1.0000	0.5%
Zn	213.857	0.6	148	60540	8951	0.9998	2.2%

*Table 4.* The calibration lines ( $y = mx+b$ , at wave length  $\lambda$  in nm), correlation  $R^2$  values, residual standard deviations (RSD), background equivalent concentrations (BEC in  $\mu\text{g dm}^{-3}$ ), and detection limits ( $C_{L(3\sigma)}$  in  $\mu\text{g dm}^{-3}$ ) obtained by a 1.00 M ammonium-acetate matrix.

	$\lambda$	$C_{L(3\sigma)}$	BEC	$m$	$b$	$R^2$	RSD
Cd	214.441	0.6	57	70051	-4008.3	1.0000	1.0%
Co	230.785	1.4	2	54840	-119.26	1.0000	0.03%
Cr	205.571	1.2	21	25579	546.52	1.0000	0.3%
Cu	324.754	2.5	213	151053	32156	0.9994	3.5%
Fe	259.940	15.8	160	258243	41379	1.0000	0.6%
Mn	257.610	0.4	2	1291505	2013	1.0000	0.02%
Ni	222.296	2.3	17	9902	-170.25	1.0000	0.3%
Pb	220.353	3.5	148	5905.2	-874.08	0.9997	2.6%
V	309.311	1.4	85	312207	26636	0.9999	1.4%
Zn	213.857	14.5	33	79775	2643.2	0.9968	1.9%

*Table 5.* The calibration lines ( $y = mx+b$ , at wave length  $\lambda$  in nm), correlation  $R^2$  values, residual standard deviations (RSD), background equivalent concentrations (BEC in  $\mu\text{g dm}^{-3}$ ), and detection limits ( $C_{L(3\sigma)}$  in  $\mu\text{g dm}^{-3}$ ) obtained by a 13 g/g nitric acid and hydrogen peroxide matrix.

	$\lambda$	$C_{L(3\sigma)}$	BEC	$m$	$b$	$R^2$	RSD
Cd	214.441	0.4	392	74770	29293	0.9980	6.6%
Co	230.785	3.5	319	50151	16009	0.9986	5.4%
Cr	205.571	1.7	328	23088	7580.7	0.9986	5.5%
Cu	324.754	0.9	343	104399	35859	0.9985	5.6%
Fe	259.940	0.7	219	216961	47594	0.9995	3.2%
Mn	257.610	0.5	211	1056725	222941	1.0000	3.6%
Ni	222.296	0.5	320	9282.3	2974.7	0.9987	5.4%
Pb	220.353	8.7	265	6483.7	1717.4	0.9991	4.4%
V	309.311	0.7	54	256488	13775	1.0000	0.9%
Zn	213.857	17.3	517	87624	45308	0.9968	8.3%

possible when the readout started from the Ar 404.442 nm reference line due to the use of 1 M ammonium acetate solution.

## 2.5. Validation

For validation of the CRM 701 sediment, the reference sample was applied. The fractionation of its element content was performed according to the modified BCR proposal [10–13] in triplicates. For the extraction of the

*Table 3.* The calibration lines ( $y = mx+b$ , at wave length  $\lambda$  in nm), correlation  $R^2$  values, residual standard deviations (RSD), background equivalent concentrations (BEC in  $\mu\text{g dm}^{-3}$ ), and detection limits ( $C_{L(3\sigma)}$  in  $\mu\text{g dm}^{-3}$ ) obtained by a 0.10 M hydroxylamine-hydrochloride matrix.

	$\lambda$	$C_{L(3\sigma)}$	BEC	$m$	$b$	$R^2$	RSD
Cd	214.441	0.9	87	47809	-4145.2	0.9999	1.5%
Co	230.785	1.4	19	44538	-856.49	1.0000	0.3%
Cr	205.571	1.4	14	18911	-258.4	1.0000	0.2%
Cu	324.754	0.9	72	163871	11765	1.0000	1.0%
Fe	259.940	0.3	1	204879	236.82	1.0000	0.2%
Mn	257.610	0.2	63	911472	57160	0.9999	1.1%
Ni	222.296	3.7	63	7505.8	471.04	1.0000	1.0%
Pb	220.353	3.9	4	4375.2	-17.636	1.0000	0.2%
V	309.311	0.2	58	260057	-15164	1.0000	1.0%
Zn	213.857	1.5	45	63846	2845.5	1.0000	0.5%

*Table 6.* Results for the BCR-fractionation of element content (in  $\mu\text{g dm}^{-3}$ ) of the CRM 701 sample.

steps		measured	certified	recovery
1 <sup>st</sup>	Cd	6.45±0.07	7.34±0.35	88%
	Co	1.68±0.06		
	Cr	1.88±0.08	2.26±0.16	83%
	Cu	44.93±0.25	49.3±1.7	91%
	Fe	57.74±2.53		
	Mn	133.17±6.52		
	Ni	12.52±0.34	15.4±0.9	81%
	Pb	1.92±0.19	3.18±0.21	60%
	V	0.06±0.23		
	Zn	160.07±4.22	205±6	78%
2 <sup>nd</sup>	Cd	3.96±0.08	3.77±0.28	105%
	Co	2.71±0.03		
	Cr	26.53±0.78	45.7±2	58%
	Cu	87.61±0.81	124±3	71%
	Fe	5648±50		
	Mn	106.99±2.90		
	Ni	19.55±0.35	26.6±1.3	73%
	Pb	92.17±2.24	126±3	73%
	V	8.50±0.09		
	Zn	98.77±2.27	114±5	87%
3 <sup>rd</sup>	Cd	1.17±0.01	0.27±0.06	435%
	Co	1.80±0.08		
	Cr	196.4±8.24	143±7	137%
	Cu	63.59±2.92	55.2±4	115%
	Fe	4652±133		
	Mn	43.65±1.25		
	Ni	24.49±0.35	15.3±0.9	160%
	Pb	60.14±0.82	9.3±2	647%
	V	5.86±0.21		
	Zn	66.44±0.62	45.7±4	145%
extra	Cd	1.38±0.01		
	Co	7.63±0.18		
	Cr	101.12±4.79		
	Cu	49.48±1.92		
	Fe	24988±805		
	Mn	302.9±3.7		
	Ni	44.50±1.36		
	Pb	12.77±0.30		
V	40.30±0.67			
Zn	127.12±1.36			

residual fraction in the extra step and for the determination of the pseudo total element content microwave supported cc  $\text{HNO}_3/\text{H}_2\text{O}_2$  digestion was applied.

Table 7. Comparison of the summarised element content (in mg kg<sup>-1</sup>) extracted in BCR steps 1-3 using certified values for the CRM 701 sample.

	steps 1-3	certified	recovery
Cd	11.58	11.38	102%
Co	6.19		
Cr	224.8	191.0	118%
Cu	196.1	228.5	86%
Fe	10358		
Mn	283.8		
Ni	56.6	57.3	99%
Pb	154.2	138.5	111%
V	14.42		
Zn	325.3	364.7	89%

Table 8. Comparison of the summarised element content (in mg kg<sup>-1</sup>) extracted in BCR steps 1-3 using pseudo-total values.

	steps 1-3+extra	pseudo-total	recovery
Cd	12.96	9.63	135%
Co	13.81	10.68	129%
Cr	325.9	290.5	112%
Cu	245.6	257.7	95%
Fe	35323	31285	113%
Mn	586.4	567.7	103%
Ni	101.0	77.2	131%
Pb	167.0	158.2	106%
V	54.68	39.20	140%
Zn	452.3	417.7	108%

### 3. Results and Analysis

The parameters of analytical calibration lines, background equivalent concentrations (BEC) and detection limits ( $C_{L(3\sigma)}$ ) obtained by different extraction matrices are summarised in Tables 2–5. It can be established that the extraction matrix solvents significantly influence the sensitivity ( $B$ ) values for all elements in the order of  $B(3^{\text{rd}}) > B(\text{extra}) > B(2^{\text{nd}}) > B(1^{\text{st}})$  as a function of steps taken. With the exception of some outliers, the residual standard deviation values are in the range of 1–2% and the detection limits are in the range of 0.5–2  $\mu\text{g dm}^{-3}$ . The outliers for Pb, Zn and Fe in certain matrices refer to neglected spectral interferences.

The results of the fractionation of the element content of the CRM 701 sample by applying the matrix matched calibration for determining the element contents in the extracts are summarised and compared with the certified and pseudo-total values in Tables 6–8. It can be seen that the metal content in BCR Steps 1–3 shows an acceptable agreement ( $< \text{mg dm}^{-3}$ ) with certified values. In the individual steps, there are larger differences for elements than are acceptable: 1<sup>st</sup> step: Pb; 2<sup>nd</sup> step: Cr, Cu, and Pb; 3<sup>rd</sup> step: Cd, Ni, Pb, and Zn.

### 4. Conclusion

Based on the results presented here, it can be concluded that the extractants applied in the BCR sequential extraction procedure cause significant matrix effects even in the case of matrix-matched multi-elemental calibration of the ICP-OES determination of element content. The sensitivities were strongly influenced by the extractant media, therefore, a much higher incident power was required to eliminate these differences to ensure conditions that are more robust. The recoveries of certified values of the CRM 701 sample were within the acceptable range when the summary of extracted amounts in the BCR Steps 1–3 was compared. Significant differences occurring in individual extraction steps between the measured and certified values refer to neglected spectral interferences. This requires a detailed study utilising the flexible line

selection possibility offered by the HORIBA Jobin Yvon ACTIVA-M instrument.

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- Ability to analyse the qualitative and quantitative characteristics of water and wastewater; creating, implementing and assessing measurement plans.
- Optimal employment and management of state-of-the-art water and wastewater treatment technologies.
- Operating, planning and managing water supply and water and wastewater treatment technologies.
- Knowledge and employment of quality assurance and technical control.
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