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Mineral constituents

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6.1 Introduction

After considering the UV–visible applications for several organic compounds and related aggregate parameters, this section shows that some inorganic constituents can also be studied either directly or indirectly with a UV–visible detection. Fig. 6.1 presents the different species studied, present under ionic forms in water and wastewater. Among the different mineral constituents potentially dissolved in water, several groups can be considered with regard to their environmental interest and nature:

	Ia	IIa		IIIa	IVa	Va	VIa	VIIa	VIII	
1	H								He	
2	Li	Be		B B ₂ O ₃ ²⁻	C CO ₃ ²⁻ , HCO ₃ ⁻ CN ⁻	N NH ₄ ⁺ NO ₂ ⁻ , NO ₃ ⁻	O O ₂ , O ₃ , H ₂ O ₂ , Oxianions	F F ⁻	Ne	
3	Na	Mg		Al	Si	P HPO ₄ ²⁻	S SO ₃ ²⁻ , HSO ₃ ⁻ SO ₄ ²⁻ , S ₂ O ₃ ²⁻ , S ₂ O ₈ ²⁻ , SCN ⁻ S ²⁻ , HS ⁻	Cl Cl ⁻ ClO ⁻ ClO ₂ ⁻	Ar	
4	K	Ca	*	Ga	Ge	As	Se	Br Br ⁻ BrO ₃ ⁻	Kr	
5	Rb	Sr	**	In	Sn	Sb	Te	I I ⁻ IO ₃ ⁻ , IO ₄ ⁻	Xe	
6	Cs	Ba	***	Tl	Pb	Bi	Po	At	Rn	
	IIIb	IVb	Vb	Vib	VIIb	VIIIb	VIIIb	VIIIb	Ib	IIb
*	Sc	Ti	V ₅	Cr CrO ⁻ CrO ₄ ²⁻ Cr ₂ O ₇ ²⁻	Mn Mn ⁻ MnO ₄ ⁻	Fe Fe ⁻ Fe ²⁺	Co	Ni	Cu Cu ²⁺	Zn
**	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
***	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg Hg ²⁺

FIGURE 6.1 Mineral constituents studies in this section (dark box) and in the library (pale box).

- The major minerals coming from the geochemical history of water include cations (Na⁺, K⁺, Ca²⁺, and Mg²⁺) and anions (HCO₃⁻, SO₄²⁻, Cl⁻, NO₃⁻). These constituents are generally present in all water with concentration from 1 milligram per liter to several grams per liter (seawater). Notice that all these ions have a natural origin, except nitrate.
- The nonmetallic minerals, associated with water pollution, are N, P, S (except sulfate) compounds. The nature and concentration of these constituents is highly dependent on the origin of the pollution (urban, agriculture, industries, etc.) and its importance and type (chronic or accidental). The concentrations corresponding are obviously variable but can reach several hundred milligrams per liter.
- The metallic constituents are from natural origin (ore) or more frequently associated with an anthropogenic pollution. Among them, toxic and heavy metals including hexavalent chromium, cadmium, and mercury must be monitored.

Almost all these ions can be determined with a colorimetric method [1].

6.2 Inorganic nonmetallic constituents

In a recent paper, Birkmann et al. [2] studied the UV spectroscopic properties of principal inorganic ionic species in natural waters in the wavelength range of 195 to 280 nm. All absorbing species were identified and the corresponding molar absorptivities were determined experimentally. No cations were found to influence the UV spectrum. Relatively high molar absorptivities were observed for iodide, bromide, and nitrate.

Actually, N and P compounds are the most important inorganic non-metallic constituents with regard to their environmental effects such as eutrophication of water bodies (lakes and rivers). Some of them are directly considered as nutrients (nitrate or phosphate), while others are nutrient precursors (ammonia, organic nitrogen, and organic phosphorous). Other constituents must also be considered, such as S compounds, mainly, because of specific environmental odor or toxicity concerns.

6.2.1 N compounds

Among water quality parameters, nitrogen is probably the most known and monitored, particularly under its more stable form nitrate. N is present in water in reduced form (organic and ammonium nitrogen) and oxidized form (nitrites and nitrates). The evolution of the N compounds depends on physicochemical and biological mechanisms occurring in natural water or all along treatment processes (Fig. 6.2).

The presence of the reduced N compounds in surface water is due to natural organic matter decomposition and, in urbanized area, to discharges coming from raw wastewater or from biological wastewater treatment plants for the ammoniacal form. These reduced compounds increase

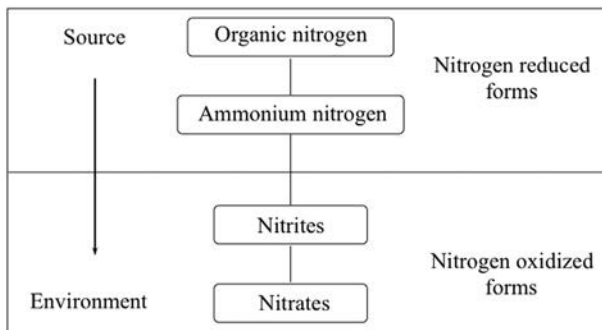


FIGURE 6.2 Main nitrogen forms in water.

the oxygen demand, resulting in the formation of final stable products as nitrate, and are toxic for fishes in rivers. Oxidized forms are one of the main eutrophication factors with phosphorous compounds and can also be toxic to human beings, through tap water. Nitrate can be chemically reduced in nitrite, which is responsible for the lack of oxygenation of cells, more particularly for babies (methemoglobinemia).

The determination of N compounds in water has given a lot of standardized analytical methods (Table 6.1), including different standard methods for nitrate determination (SM 4500 nitrogen-nitrate) [3].

Among these methods, the colorimetric and spectrophotometric ones are the most widely used for field or lab monitoring. If colorimetric methods based on continuous flow analysis (CFA), flow injection analysis (FIA), or sequential injection analysis (SIA) are available as standard methods [2], UV procedures are also standardized and largely implemented in online or field-portable instruments mainly for nitrate monitoring

TABLE 6.1 Selection of standard methods for nitrate determination in water.

Method	Principle	Range	Observations/interference
4500-NO ₃ ⁻ B	UV spectrophotometry	0.2–11 mg L ⁻¹ NO ₃ ⁻	Organic matter and colloids interference
4500-NO ₃ ⁻ C	Second-derivative UV	0.5–2.5 mg L ⁻¹ NO ₃ ⁻	Pathlength 10 mm screening method
4500-NO ₃ ⁻ D	Nitrate electrode	0.14 to 1400 mg L ⁻¹	3 < pH < 9 constant
4500-NO ₃ ⁻ E	Colorimetry Cadmium reduction	0.01–1.0 mg L ⁻¹ NO ₃ ⁻	Suspended matters, metals, oils grease, color
4500-NO ₃ ⁻ F	Automated Cd reduction	0.05–10 mg L ⁻¹ NO ₃ ⁻	Turbidity, color
4500-NO ₃ ⁻ H	Automated hydrazine reduction	0.05–10 mg L ⁻¹ NO ₃ ⁻	Sulfide, color
4500-NO ₃ ⁻ I	Cd reduction Flow injection	0.01–2.0 mg L ⁻¹ NO ₃ ⁻	Particles, residual chlorine, metals
4500-NO ₃ ⁻ J	Enzymatic reduction	0.05–10 mg L ⁻¹ NO ₃ ⁻	Particles
4110-NO ₃ ⁻ B	Ion chromatography	0–12 mg L NO ₃ ⁻	Particles
4140-NO ₃ ⁻ B	Capillary electrophoresis	0.1–50 mg L ⁻¹ NO ₃ ⁻	Buffering Particles
ISO 7890	Colorimetric method	0.03–0.2 mg L ⁻¹ NO ₃ ⁻	Colored sample

in water and wastewater. Ion chromatography or capillary electrophoresis can also be used for nitrate determination. In their review, Azmi et al. [4] proposed some membrane techniques for the improvement of the capabilities of various nitrate detection methods. A recent review [5] on spectroscopic methods for the determination of nitrite and nitrate in environmental samples concluded that spectroscopic methods were successful if water sample contains little or no organic matter. Another work on recent progress in sensing nitrate, nitrite, phosphate, and ammonium in aquatic environment [6] recommended that direct nitrate detection is beneficial and can be achieved by a UV spectrophotometric-based sensor. For other forms of nitrogen (ammonia or organic nitrogen), CFA, FIA, and SIA as well as other methods based on the Kjeldahl method can be considered [7–9]. For total Kjeldahl nitrogen (TKN), including organic and ammoniacal nitrogen, the reference procedure [10] needs mineralization and distillation steps and the use of a final colorimetric or titrimetric determination. In this context, an alternative approach using UV spectrophotometry, either directly or after some simple treatment steps for the final detection, was proposed.

6.2.1.1 General procedure

This simple methodology, called UV/UV method, was designed for the quick determination of the different forms of nitrogen in water, nitrite, nitrate, ammonium, and TKN [11]. The general procedure is based on several steps (Fig. 6.3) but includes a UV determination of the oxidized forms and one or two UV photooxidation step(s) for the

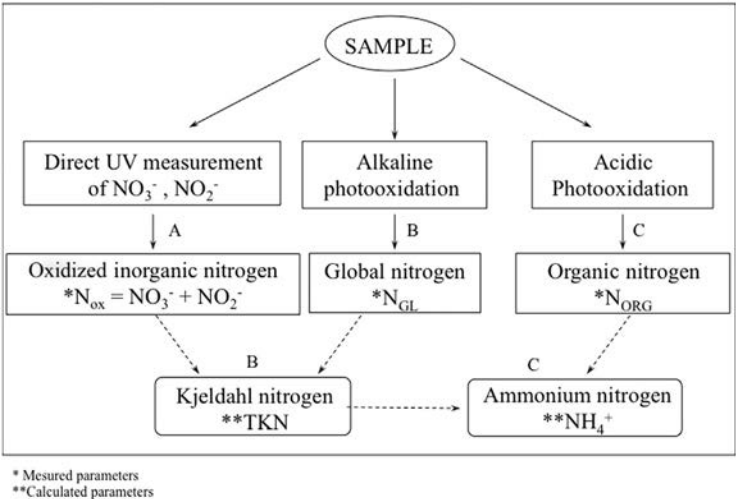


FIGURE 6.3 General UV/UV procedure for N compound determination [11].

mineralization of the reduced forms. Phosphorus determination is also possible with this method. Neither filtration nor acidification of the sample is needed.

First of all, the oxidized forms of inorganic nitrogen (nitrate, nitrite) are detected by direct UV spectrophotometry (way A). Second, the sample is photooxidized with a photo-digester (way B), in the presence of an alkaline oxidant solution (potassium peroxodisulfate buffered to pH 9). Under the influence of UV radiation (in this case, a simple low-pressure mercury lamp emitting at 254 nm), the global nitrogen is converted into nitrate. Then, TKN can be calculated from the difference between the concentration of global nitrogen and the one of the oxidized forms previously determined.

In the third part of the general procedure (way C), the sample is photooxidized in the presence of an acidic oxidant solution (pH 2 with sulfuric acid 20%). In these conditions, only organic nitrogen is converted into nitrate. The difference between the concentration of TKN previously calculated and that of organic nitrogen leads to the calculation of ammonium nitrogen concentration.

Thus all nitrogen forms (N_{ox} , N_{org} , NH_4^+ , and TKN) present in water and wastewater can be rapidly and simply determined by UV spectrophotometry.

6.2.1.2 Nitrate measurement

The determination of nitrate is certainly the most important application of UV spectrophotometry for water quality monitoring. The reason is that the spectra of nitrate solutions are very characteristic between 200 and 400 nm in function of the concentration (Fig. 6.4). Nitrate ion is rather sensitive to UV absorption with a half Gaussian shape for low concentration (between 0.5 and 15 mg $NO_3\text{-L}^{-1}$ without dilution for 10 mm pathlength).

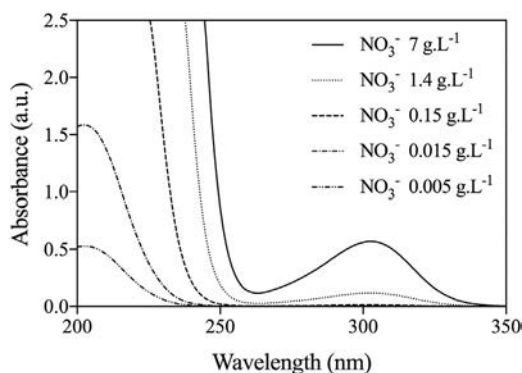


FIGURE 6.4 UV spectra of nitrate solutions.

When the concentration increases, an absorption peak appears around 310 nm from $0.2 \text{ g NO}_3\text{-L}^{-1}$, without dilution for 10 mm pathlength. In between, no particular shape exists, except the saturation wall for short wavelengths. This typical response is exploited for nitrate determination with different wavelength ranges in function of the expected concentration. Actually, Simeon et al. [12] reported the existence of two forms of nitrate ions in relatively concentrated solutions (around 5 g L^{-1}), with a very slight difference in their UV spectra. They also showed that depending on the associated cation, nitrate ion associated as ion pairs can give different UV response at high salt concentrations for transition-metal ions compared to that of nontransition cations. That could be a consequence of different types of cation–anion interactions [13].

A lot of works have been published for more than 50 years on the use of UV spectrophotometry for nitrate determination in water, with more than 35,000 papers since 2017 (Google Scholar database). The proposed methods can be classified according to the exploitation method used, among those presented in Chapter 2:

- The earlier methods are based on simple absorptiometry at one or two wavelength(s) [14–17]. Generally, the use of one absorbance value between 205 and 220 nm, compensated by another one between 250 and 300 nm, is proposed. For example, a screening method based on the measurement of absorbance at 220 nm was standardized [2], with a correction for dissolved organic matter from a second measurement at 275 nm. For high concentrations of nitrate (in the case of industrial application), a simple absorptiometric method can be envisaged at 310 nm.
- The second group focuses on the interest of the calculation of the second derivative or its estimation with a three-wavelengths measurement, around 220–225 nm [18–21]. A standardized method using second derivative was also proposed [2]. These methods are less sensitive to interferences than the first group (supposing that the slope of the UV spectrum of interferences is constant) and can be run on most UV sensors and lab spectrophotometers.
- Other efficient methods exploit the entire UV spectrum between 200 and 350 nm [22–25], through multiwavelengths procedures. They are based either on partial least squares (PLS) algorithm [25] or on the semideterministic deconvolution procedure or UVSD (UV spectral deconvolution) method [23] described in Chapter 2. These methods give excellent and very rapid results compared to classical analysis, such as colorimetry, but need a specific software for data processing.

An example of the comparison of a second-derivative UV method, with a standard one (NF EN ISO13395) using CFA and colorimetry at 543 nm, is given in Fig. 6.5 [18]. The validation was carried out on 580 freshwater samples. The adjustment between the measured

concentration of nitrate and the estimated values [by second-derivative absorbance (SDA) at 226 nm] gave a coefficient of determination R^2 greater than 0.99, without filtration of samples.

6.2.1.3 Nitrite measurement

As for nitrate, nitrite concentration can be measured by FIA or SIA [7,8]. Concerning its UV absorption characteristics, nitrite ion also presents a specific absorption in the far UV region of spectrum, slightly different from the one of nitrate (Fig. 6.6). A first peak appears, as for nitrate, at 210 nm for relatively low concentrations (actually, rather high with respect to regulation limits). This first peak is shown from concentrations greater than 0.5 mg $\text{NO}_2^- \text{L}^{-1}$ for a 10 mm pathlength. A second peak appears at

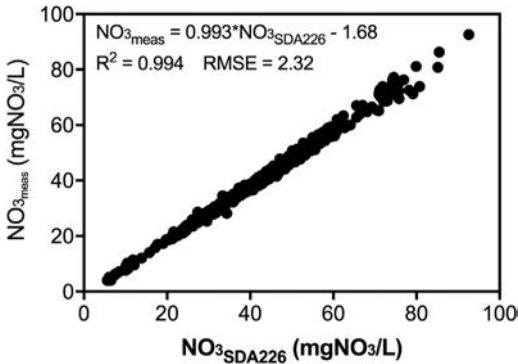


FIGURE 6.5 Relation between measured and estimated (from SDA226) NO_3 concentrations for 580 freshwater samples [18].

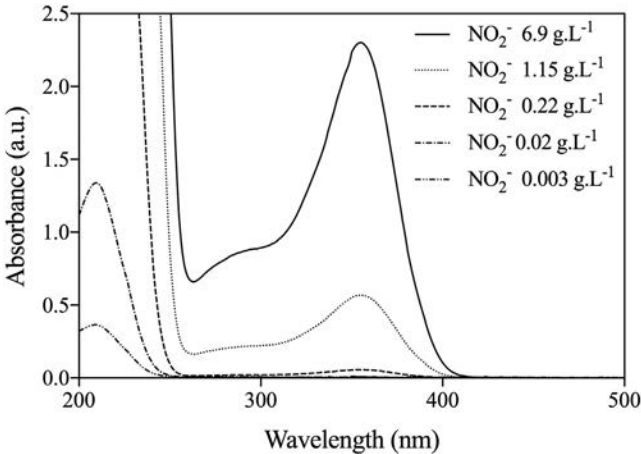


FIGURE 6.6 UV spectra of nitrite solutions.

355 nm when concentration increases from $0.2 \text{ g NO}_2^- \text{ L}^{-1}$, without dilution for a 10 mm pathlength, as for nitrate. However, contrary to the nitrate spectrum, a shoulder at 280–300 nm accompanies the second peak. This difference can be used for the analysis of nitrate and nitrite in mixture. Actually, as nitrite is very unstable and is easily oxidized into nitrate, its concentration in water is often very low. Thus UV spectrophotometry seems to be useful, for example, for industrial applications where nitrite concentration may be higher than $0.5 \text{ mg NO}_2^- \text{ L}^{-1}$ (in agrofood industry wastewater, for example). Based on the spectra characteristics of nitrite solutions (Fig. 6.6), the expected figures of the UV method are a measuring range of 1 to $30 \text{ mg NO}_2^- \text{ L}^{-1}$ with a detection limit of $1 \text{ mg NO}_2^- \text{ L}^{-1}$.

6.2.1.4 Total Kjeldahl nitrogen measurement

Concerning the determination of nitrogenous organic compounds, several methods are available often coupled with phosphorous organic compounds [26], but the measurement of the TKN remains the main procedures. Several methods using UV radiation for the mineralization of samples have been proposed in order to simplify the reference Kjeldahl procedure [27]. These methods generally require a classical low-pressure mercury lamp emitting at 254 nm. The use of the far UV radiation of the Hg lamp (185 nm) is made possible by using transparent Suprasil quartz and leads to the improvement of the photodegradation process as compared to the Kjeldahl method (5 to 10 hours for Kjeldahl method; 2 to 3 hours for direct UV). The use of a strong oxidant with a far UV radiation leads to the drastic decrease of the reaction time (5 to 10 minutes) [28]. The reaction can be followed by UV spectrophotometry (Fig. 6.7) with the disappearance of UV spectra of initial compounds and the appearance of that of final compound (nitrite and

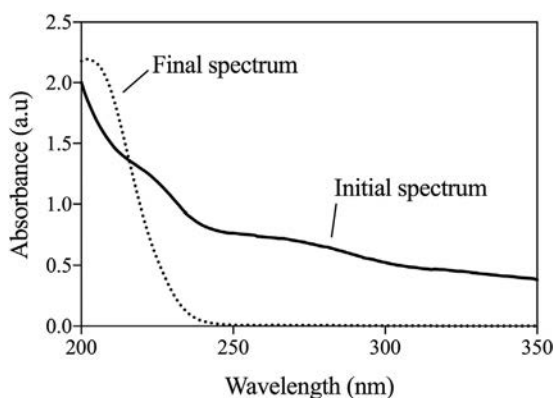


FIGURE 6.7 Initial and final spectrum during photodegradation of an urban wastewater sample.

nitrate). The quantification is possible with the semideterministic approach (Chapter 3) by using two sets of reference spectra for the restitution of spectra acquired during the photodegradation. The first basis is the one defined for the estimation of aggregated parameters (see Chapter 5) in water and wastewater. The second basis is simpler as it can include only nitrate and nitrite spectra.

For TKN determination, the photooxidation is carried out in the presence of an oxidant solution (potassium peroxodisulfate $K_2S_2O_8$ buffered to pH 9). In this case, both organic and inorganic nitrogen compounds are converted into nitrate. The concentration of TKN is equal to the difference between nitrate measured after photooxidation ($[NOX]_f$), and nitrate measured before ($[NOX]_i$):

$$[TKN] = [NOX]_f - [NOX]_i$$

The procedure was first applied on model compounds. Table 6.2 displays the results of the determination of the nitrogen concentration of various N-containing compounds. The conversion into nitrate from all compounds is quantitative, whatever the concentration, and the conversion times are very short, around 5 minutes of irradiation time [28].

The conversion into nitrate is possible under UV irradiation without the presence of chemical oxidant, with an increase of the reaction time (around 2 hours).

The validation of the procedure has been carried out from the UV/UV estimation of TKN concentration of 80 samples of urban and industrial wastewater. TKN standard method was used as reference method, and the results are shown in Fig. 6.8. A good adjustment can

TABLE 6.2 Percentage of conversion into nitrate from N compounds.

Compounds ^a	UV method ^b (percentage recovery)	Compounds ^a	UV method ^b (percentage recovery)
Urea	95–100	Glycine	90–95
N-acetyl-glucosamine	95–100	EDTA	80–90
4-aminophenol	95–100	m-toluidine	80–90
2-nitrophenol	90–100	Atrazine	80–90
4-nitrophenol	90–100	Aniline	70–80
3-aminophenol	90–100	Glutamic acid	70–80

^aConcentration between 5 and 50 mg N/L, pH 9.

^b5 min irradiation time.

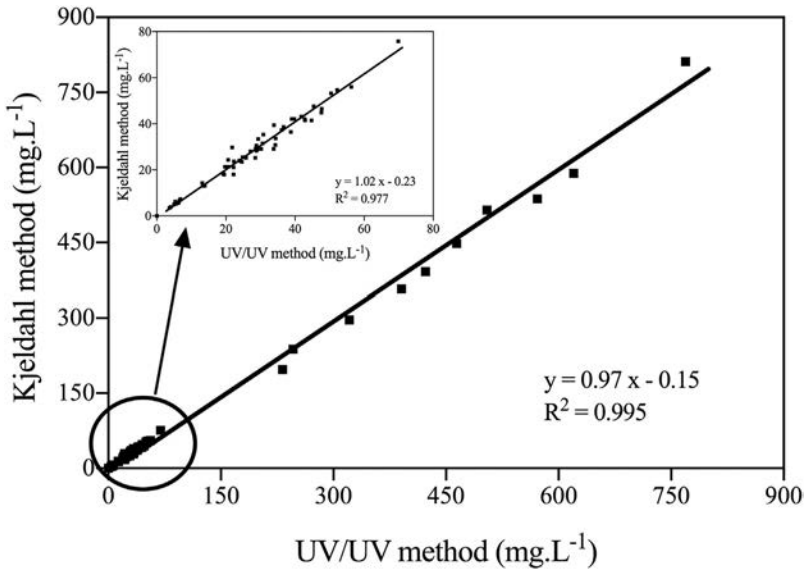


FIGURE 6.8 TKN measurement comparison between the Kjeldahl and the UV/UV methods [28]. TKN, total Kjeldahl nitrogen.

be observed between the results for a wide concentration range. From few mg N L^{-1} to several hundred mg N L^{-1} , the comparison between the two methods is good, as well as the precision.

Thus the UV/UV method can be used as an alternative way for the reference TKN method.

6.2.1.5 Ammonium measurement

Ammonium determination is usually carried out with CFA, FIA, or SIA [8,9]. With the UV/UV procedure two steps of photooxidation are needed [29]. The first one allows the measurement of TKN as shown above. Then, a second one is carried out in the presence of an oxidant solution (potassium peroxodisulfate $\text{K}_2\text{S}_2\text{O}_8$), without buffer. In these particular conditions (acidic medium), only organic nitrogen compounds are converted into nitrate, as will be explained afterward.

The concentration of ammonium can be calculated by the difference between the TKN-estimated concentration ([TKN]) and the one of organic nitrogen ($[\text{N}_{\text{ORG}}]$), taking into account an eventual dilution. The relation is the following, where all concentrations must obviously be expressed in the same unit (mg N L^{-1}):

$$[\text{NH}_4^+] = [\text{TKN}] - [\text{N}_{\text{ORG}}]$$

A validation was carried out for 80 industrial wastewater samples analyzed with both a standard method (capillary electrophoresis) and the UV/UV one (Fig. 6.9). A good adjustment can be observed between the results for a wide concentration range (1–100 mg N L⁻¹) and the detection limit is 1.2 mg NH₄⁺ L⁻¹, confirming that this method is only suitable for high ammonium concentrations.

The presented UV/UV method allows the simple and reliable determination of all nitrogen forms by using the same technique. Moreover, the total reaction time is rather short as a maximum of 40 minutes is required for all measurements (Table 6.3).

Some comments can be made concerning the process, and more precisely the impact of the pH on the photodegradation results. Actually, the photooxidation of nitrogenous organic compounds leads to the cleavage of C–N bond resulting in the formation of ammonium radical

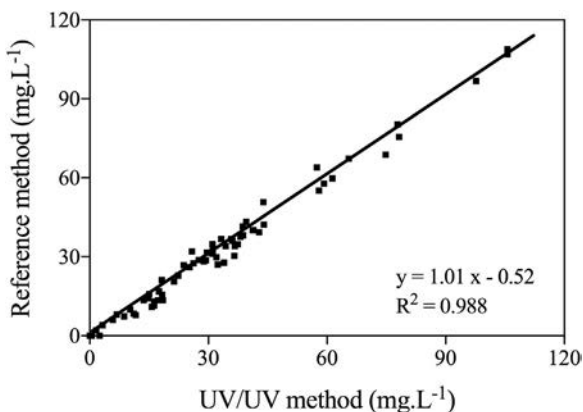


FIGURE 6.9 Comparison of ammonium determination for industrial wastewater (reference method is capillary electrophoresis).

TABLE 6.3 Time analysis (in minutes) for the determination of nitrogen forms.

	NO _x	N _{org}	N _{global}	TKN	NH ₄ ⁺
Photooxidation	<i>no</i>	10–15	10–15	<i>no</i>	<i>no</i>
Measurement	1	1	1	<i>no</i>	<i>no</i>
Exploitation	1 (dec)	1 (dec)	1 (dec)	1 (cal)	1 (cal)
Total	2	10–15	10–15	1	1

Note: *dec*, deconvolution; *cal*, calculation.
TKN, total Kjeldahl nitrogen.

NH_4^+ [30]. A hydrolysis step follows this reaction in order to obtain first ammoniacal nitrogen and second the final oxidized forms of nitrogen, that is, nitrite and nitrate.

Moreover, the pH value allows the specific reactivity of organic and inorganic nitrogen. The pH effect can be studied from the comparison of the photooxidation of urea (as organic nitrogen) and ammonium chloride (as inorganic nitrogen). It appears that the conversion of urea is weakly modified by the pH and varies between 80% and 95%, whatever the pH value, whereas the conversion yield from the ammonium nitrogen is very weak in acidic medium and becomes quantitative for basic conditions [31].

The presence in wastewater of several organic (solvent) and inorganic (carbonates) compounds may interfere with the photooxidation because they are scavengers, inhibiting the action of oxidant radicals. Their action can decrease the conversion yield to 50% in function of the concentration [26].

6.2.2 P compounds

Two reviews about phosphorus determination in natural waters were published recently [32,33]. Considering the role of excess phosphorus in eutrophication and algae blooms, the monitoring of dissolved phosphorus in water and wastewater is important. The main analytical methods for the determination of phosphorus are spectrophotometric ones with the formation of a phosphomolybdate complex. The phosphorus compounds in water and wastewater concern not only some organic forms (natural or anthropic) but also orthophosphate ion and acid hydrolyzable phosphate (condensed phosphate) (Fig. 6.10).

Standard methods [2] used for the determination of total phosphorus include several procedures. Orthophosphates (PO_4^{3-} and associated forms) are determined by colorimetry, ion chromatography, or spectrophotometry (UV-visible). Acid hydrolysis allows the transformation of polyphosphates

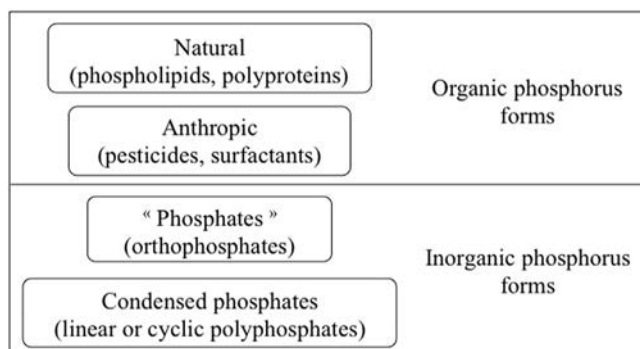


FIGURE 6.10 Phosphorus forms in water.

in orthophosphates, which are measured by one of the mentioned methods. Finally, a chemical digestion, followed by the determination of resulting species (PO_4^{3-}) allows the measurement of organic phosphorus forms. Procedures are time-consuming (more than 5 hours) and require strong conditions (acidic medium, high temperature, and catalyst).

Some improvements have been proposed, such as the use of photooxidation as an alternative to chemical digestion, as it has been successfully used for similar applications [32,34,35] particularly for flow analysis. In order to minimize the photooxidation time, the UV light source (high-, medium-, or low-pressure mercury lamp) can be associated with oxidants (hydrogen peroxide or potassium peroxodisulfate). Generally, the converted forms (orthophosphates) are determined by off-line analysis but can also be measured by CFA, FIA, or SIA.

In this section, a simple procedure, based on the use of a UV photooxidation module (previously described) and a UV–visible measurement, is presented [36]. Another procedure, based on the use of the alternative vanadomolybdophosphoric acid method with a UV-LED detection at 380 nm can also be envisaged [37].

6.2.2.1 General procedure

As previously mentioned, phosphorus compounds are commonly classified into orthophosphates (PO_4^{3-}), acid-hydrolyzable (condensed) phosphates, and organic phosphates. It must be noticed that acid-hydrolyzable phosphates (as pyrophosphates) are negligible in sewage [38]. The general procedure illustrated in Fig. 6.11 includes two main steps: an indirect UV–visible measurement (for PO_4^{3-}) and a

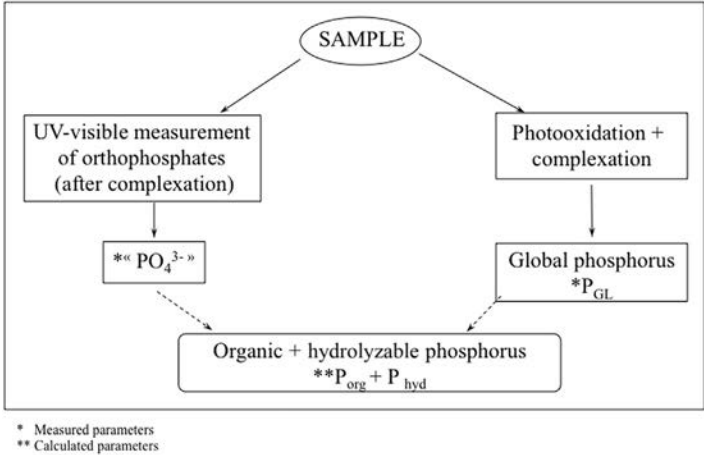


FIGURE 6.11 Speciation of phosphorus in wastewater.

photooxidation step followed by a UV–visible measurement for global phosphorus determination (P_{GL}). First, orthophosphates are determined by the spectrophotometric measurement of the phosphomolybdate complex (formed with addition of ammonium molybdate 40 g L^{-1}) using the spectrum deconvolution method (Chapter 3).

Then, an oxidant solution (40 g L^{-1} potassium peroxodisulfate $K_2S_2O_8$) is added to the sample for the photoconversion (15-minute irradiation times) of the organic phosphorus forms into orthophosphates. Orthophosphates are then determined by UV–visible spectrophotometry.

The procedure allows the measurement of orthophosphate (PO_4^{3-}) and global phosphorus (P_{GL}). The determination of the sum of organic and hydrolyzable phosphorus ($P_{ORG} + P_{hyd} = P_{GL} - PO_4^{3-}$) is then possible.

6.2.2.2 Orthophosphates

The measurement of orthophosphates is generally assumed thanks to the phosphomolybdate complex formation produced and detected in a flow analysis system (CFA, FIA, or SIA). For UV determination, the deconvolution procedure [23] can be used with a basis of reference spectra corresponding to the molybdate solution (2.4 g L^{-1}) and to the phosphomolybdate complex obtained from 10 mg L^{-1} of orthophosphate. Notice that in this case the use of a simple multicomponent procedure may be sufficient. The quantification is carried out between 380 and 450 nm. The orthophosphate concentration is given by the product of the phosphomolybdate complex coefficient by the concentration of the corresponding reference spectrum.

Fig. 6.12 shows the comparison between the orthophosphate concentration estimated by deconvolution and the concentration measured by ascorbic

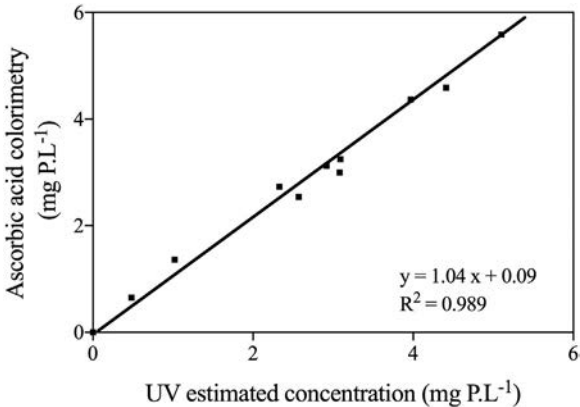


FIGURE 6.12 UV estimation of orthophosphate concentration [9].

acid colorimetry as a reference method. The UV-estimated concentrations are in good agreement with the expected ones and then can be used as an alternative to the standardized method. Even if the characteristics of the method are interesting with a detection limit of $10 \mu\text{g PO}_4 \text{ L}^{-1}$, this must be lowered up to $5 \mu\text{g PO}_4 \text{ L}^{-1}$ for trace analysis. Classical methods based on flow analysis techniques are more adapted in this case.

6.2.2.3 Total phosphorus

As orthophosphates, total phosphorus is generally determined by flow analysis (CFA, FIA, or SIA). Inductively coupled plasma with optical emission spectroscopy (ICP-OES) can also be used for detection if concentrations are sufficiently high [32] as well as atomic absorption spectroscopy (AAS). The determination of total phosphorus needs a photooxidation step in the presence of an oxidant (potassium peroxodisulfate, for example) allowing the transformation of all phosphorus forms into orthophosphates that are complex (with a molybdate solution) when they are formed [36].

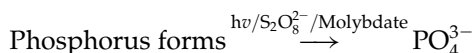


Table 6.4 displays the results for the determination of the orthophosphate concentration from the photooxidation of various P-containing compounds. The molybdate solution (1.5 mL) is introduced into the reactor in order to follow the phosphomolybdate complex formation. The conversion yields are quantitative using irradiation time no longer than 15 minutes.

The UV/UV–visible method was applied for the determination of total phosphorus from raw effluents. The results were compared with those obtained by atomic absorption spectrometry (AAS) as the reference method (Fig. 6.13) and the comparison showed a good correlation

TABLE 6.4 Conversion yields obtained from organic phosphorus compounds.

Compounds ^a	Conversion yields ^b	Compounds ^a	Conversion yields ^b
N (phosphonomethyl) glycine	100	Glucose-1-phosphate	100
Mevinphos	100	AMP	90
Dichlorvos	100	ADP	90
Dibrom	100	ATP	85
Tris (2-chloroethyl) phosphate	90	–	–

^aConcentration between 1 and 10 mg L⁻¹.

^b10–15 min irradiation time.

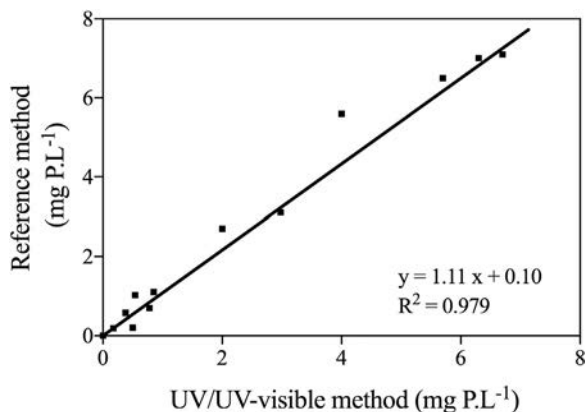


FIGURE 6.13 Comparison of total phosphorus measurement by the atomic absorption and UV/UV-visible methods.

($R^2 = 0.979$). The detection limit was 0.05 mg P L^{-1} for a range of 0.05 to 10 mg P L^{-1} .

The UV/UV system was described as an efficient method for the measurement of phosphorus in wastewater. According to the experimental conditions of photooxidation or UV measurement, it is possible to evaluate the major part of phosphorus forms (oxidized, organics, inorganics, and hydrolyzable) and total phosphorus.

Finally, a recent method for the simultaneous determination of total dissolved nitrogen and total dissolved phosphorus in natural waters with an online UV and thermal digestion was proposed [27].

6.2.3 S compounds

Sulfur occurs in wastewater in various forms. Most of the time, anoxic conditions in urban sewer lead to the production of hydrogen sulfide, but the presence of sulfur compounds is more often related to industrial discharges, mainly from refineries or petrochemical plants.

Some petroleum contains elemental sulfur, which can occur as hydrogen sulfide (H_2S) and carbonyl sulfide (COS). Sulfur is also present in a wide range of hydrocarbons, largely as mercaptans, organic sulfides, and thiophene derivatives [39]. Sulfur compounds tend to be concentrated in the higher boiling fractions of petroleum, are generally corrosive to metals, and may poison various catalysts. Stripping water is responsible for the presence of sulfide and mercaptans into crude oil refinery wastewater.

Sulfide under dissolved H_2S form is toxic for fish and other aquatic organisms and can be responsible for the decrease of wastewater

treatment plants' efficiency. Therefore its concentration needs to be controlled, especially in wastewater from crude oil refineries.

Inorganic sulfur compounds are numerous and can be classified, as for nitrogen, between reduced and oxidized forms. Table 6.5 lists these compounds and their main origin areas, when they are found in water or wastewater.

The reduced forms of sulfur are also called total sulfides, as they are all associated with the acido-basic equilibrium of hydrogen sulfide (at 25°C):

$$pK_a(H_2S/HS^-) = 7.05$$

$$pK_a(HS^-/S^{2-}) = 12.92$$

Considering the pKa values, the predominant form is the bisulfide ion (HS^-), since the molecular form of hydrogen sulfide (H_2S) is volatile. This observation is true if the pH value of water or wastewater is about 7.

The corresponding UV spectra, the shape of which depends on the pH value, are shown in Fig. 6.14. An important peak can be noted at 231 nm, related to the presence of hydrogen sulfide and corresponding to the bathochromic shift between the two forms of first acidity (notice that the spectrum of acidic solutions are much less absorbing because of the hypochromic effect and volatility of hydrogen sulfide).

From an analytical point of view, total sulfide includes dissolved H_2S and bisulfide ion HS^- , which are in equilibrium with hydrogen ions. For pH values of wastewater, the S^{2-} form is generally negligible, less than 1% of the dissolved sulfide under pH 10.

TABLE 6.5 Main sulfur species related to water and wastewater.

Sulfur species	Formula	Origin or use
Sulfide ion	S^{2-}	Industrial
Bisulfide ion	HS^-	Industrial/OM reductive degradation
Hydrogen sulfide	H_2S	OM reductive degradation (gas)
Thiosulfate ion	$S_2O_3^{2-}$	Chemical reagent (titration)
Tetrathionate ion	$S_2O_5^{2-}$	Industrial
Sulfate ion	SO_4^{2-}	OM oxidative degradation
Peroxodisulfate ion	$S_2O_8^{2-}$	Chemical reagent (digestion)

OM, organic matter.

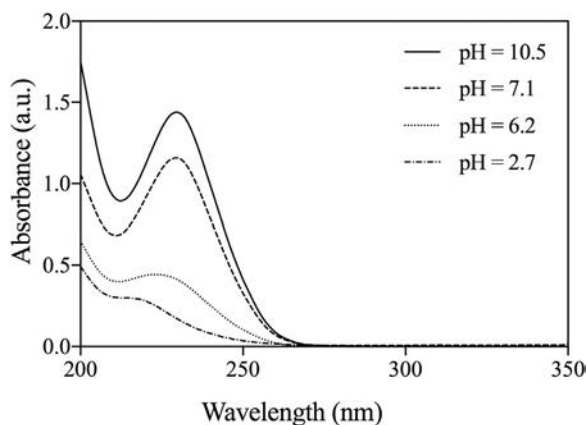


FIGURE 6.14 UV spectra of a sulfide solution (HS^- 10 mg L^{-1}).

Sulfide can be determined in different media, using various techniques [40,41], including flow analysis systems (FIA and SIA). Three main methods are commonly used for the determination of sulfide in solution:

1. the colorimetric method, with methylene blue, based on the reaction of sulfide, ferric chloride and dimethyl-*p*-phenylenediamine to produce methylene blue, which absorbs at 664 nm [2];
2. the iodometric method based on the oxidation of sulfide by iodine in acidic solution followed by a back titration with sodium thiosulfate solution;
3. the potentiometric method using a selective silver electrode.

Fig. 6.15 shows UV spectra of refinery wastewater containing mineral sulfide (with corresponding dissolved organic carbon (DOC) around 1000 mg C L^{-1}). The value of samples' pH is around 9. The characteristic peak of bisulfide ion appears clearly on the UV spectra (231 nm), despite the matrix sample. The intensity of the UV band is related to the concentration of sulfide.

The use of a UV spectrophotometric procedure can also be proposed as an alternative method for the determination of inorganic sulfide in water and wastewater. A first method, based on the use of a multiwavelengths procedure, has been proposed for natural water [42]. The interferences are modeled from an exponential function and the simultaneous determination of total sulfide and iodide is possible. A second method integrates the semideterministic deconvolution procedure or UVSD method [23,36]. The potentiometric method will be chosen as reference for the validation of this last procedure. The UV quantification is carried out by deconvolution (see Chapter 3) between 205 and 320 nm . Raw samples were diluted four times

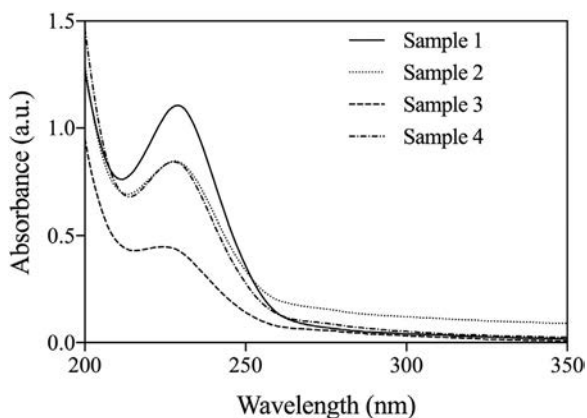


FIGURE 6.15 Refinery wastewater UV spectra (dilution 25), with sulfide (88, 39, 23, and 45 mg S L⁻¹, respectively).

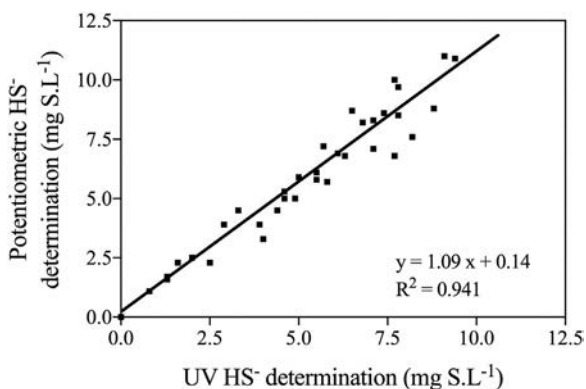


FIGURE 6.16 Validation of sulfide UV determination.

to prevent the UV signal saturation for a 10-mm quartz cell. Sulfide concentration is given by the product of the contribution coefficient of sulfide reference spectrum (replacing nitrate in the previous set) and the corresponding concentration, affected by the dilution factor.

About 40 wastewater samples from refineries were used for the validation of the UV method [36]. Fig. 6.16 shows a good linear adjustment between the measured concentration by the potentiometric method and UV determination of sulfide. The characteristics of the UV method (without dilution) are a concentration range between 0.5 and 15 mg S L⁻¹ and a detection limit of 0.5 mg S L⁻¹.

Some compounds absorbing close to 231 nm sometimes present in raw wastewater samples can interfere with sulfide spectra. Several

compounds, for example, *p*-chlorophenol (absorption at 227 nm), anionic surfactant, RBS commercial product (absorption at 223 nm), and 1-propanthiol (absorption at 239 nm), were tested, and the results show low interference values to the studied compounds [36]. The error of restitution by deconvolution was 5% at maximum with the highest interference associated with anionic surfactant (leading to an error of 4.3%).

The UV method has been described as a simple and reliable procedure for the determination of sulfide in wastewater. Compared with some reference methods, it is less sensitive but do not need any sample preparation (pretreatment, filtration, etc.) and is unaffected by interferences (salinity, suspended matter, organics compounds, etc.).

Recently, two UV-based methods were proposed. The first one [43] is a fast determination of the main reduced sulfur species (sulfides, sulfites, and thiosulfates) in aquatic systems by a direct and second-derivative spectrophotometric method, based on the comparison of SDA spectra of the same sample at different pH (9.2, 4.7, and 1.0) and selected absorption wavelengths (250 and 278 nm). The second method is a field method for the determination of trace levels of sulfite in natural waters [44], based on automated dispersive liquid–liquid microextraction (DLLME) coupled with ultraviolet–visible spectrophotometry. The automated DLLME system was designed around a single syringe pump coupled with a multiposition valve. The method allows the precise determination of trace levels of sulfite with a detection limit of $1 \mu\text{g L}^{-1}$.

Concerning the determination of sulfate ion, there exist several standard methods [45], such as the ion chromatographic method, capillary ion electrophoresis (for low concentrations), and gravimetric methods for concentration above 10 mg L^{-1} . Moreover, two procedures used a final optical detection, one based on turbidimetry after precipitation with Baryum chloride (measurement of the absorbance at 420 nm) and the other based on the automated methylthymol blue method (final detection at 460 nm).

Simple colorimetric reactions are not available for sulfate analysis and sulfate ion does not absorb in the UV–visible range. However, a recent spectrophotometric method was proposed by Salem and Draz [46] thanks to the synthesis of PEG-25 stabilized silver nanorods used as sensing probes for the colorimetric determination of sulfate from the decrease of the peak around 460 nm.

6.2.4 Cl compounds

Chlorine compounds are potentially numerous, as sulfur ones, with several oxidation states. Nevertheless, there is a great difference between the two elements, because all oxidized forms of chlorine compounds are generally unstable in solution contrary to sulfate ion. Some of them, for

example, chlorine itself (Cl_2), hypochlorite ion (ClO^-), and chlorine dioxide (ClO_2), are used as oxidant agents for tap water production or swimming pool treatment.

6.2.4.1 Chloride

Chloride ion is one of the major inorganic anions in water and wastewater because it is the more stable form of chlorine in solution. Chloride concentration is very variable and can be high not only in seawater. It is used for domestic purpose, but rather often for industrial processes. In some applications, the resulting concentration in wastewater can be important and greater than 1 g L^{-1} (food and chemical industry, for example).

Fig. 6.17 presents several spectra of industrial water containing chloride as compared to seawater. In all cases, the shape of chloride signal can be observed, characterized by a very high increase of absorbance values below 210–220 nm, always convex, in contrast to nitrate. The difference between industrial cooling water UV spectra and seawater spectrum is that the first ones show a residual diffused absorption for wavelengths greater than 220 nm due to the presence of organic matter at a higher concentration than in seawater.

Several methods can be used for the determination of chloride in water [2]. The argentometric and mercuric nitrate methods are based on the titration of chlorine in the presence of an indicator. Experimental procedures are easy, but many substances may interfere with the results. There are also other methods such as potentiometry, capillary electrophoresis and other automated colorimetric methods implemented in flow analysis systems (CFA, FIA, or SIA).

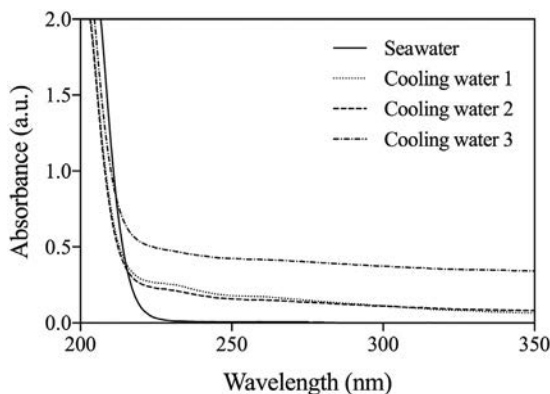


FIGURE 6.17 UV spectra of cooling and seawater (dilution 5). Chloride concentrations are between 15 and 22 g L^{-1} .

Taking into account its UV absorption signal, chloride concentration can be quickly estimated by UV for high concentrations (above 500 mg L^{-1}). The semideterministic method (Chapter 3) used for UV spectra exploitation can be applied by integrating the spectrum of a chloride solution on the basis of reference spectra. The concentration is then calculated by multiplying the corresponding chloride concentration with the contribution coefficient of the chloride spectrum.

For a wavelength window between 200 and 320 nm, the method can be applied for a concentration range of $0.5\text{--}6 \text{ g L}^{-1}$ with a detection limit of 0.5 g L^{-1} . A comparison between this UV procedure and the reference potentiometric method has been carried out on 110 industrial samples. Fig. 6.18 shows the quality of the adjustment between the two sets of results.

6.2.4.2 Hypochlorite

Chlorine may also be found in water under the hypochlorite ion form, which is a strong oxidant used for water and housing disinfection. It is used for tap water production as well as for swimming pool water treatment or, in some cases, for the oxidation of odorous compounds. This product (commonly found as “Eau de Javel” or bleach solution) also has a persistent disinfecting action as long as hypochlorite remains in the solution. The residual concentration must thus be sufficient, but not in large excess, because of the formation of organohalogeno compounds such as chloramines, which are responsible for eye irritations and can even be toxic.

The presence of hypochlorite ion can easily be monitored by UV spectrophotometry for relatively high concentrations, because its UV spectrum presents, contrary to the one of chloride ion, an important

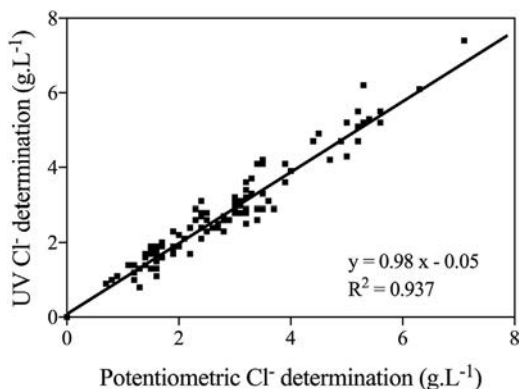


FIGURE 6.18 Comparison of UV estimation of chloride in industrial water with the potentiometric method.

Gaussian-like peak centered on 290 nm. Applications for oxidation process control using hypochlorite, gaseous chlorine, or chlorine dioxide are thus possible using UV spectrophotometry. The spectrum exploitation is possible with the semideterministic method (by including the corresponding reference spectrum, as previously) but a simpler absorptiometric procedure can be used at 290 nm, if interferences (organic compounds, suspended solids, etc.) are negligible.

Fig. 6.19 shows some examples of samples of swimming pool and deodorization water. A comparison has been carried out between the concentration obtained by UV spectrophotometry, either simple absorptiometry at 290 nm or with the semideterministic approach. Fig. 6.20 shows the right adjustment for the results for 10 samples of real water with standard additions of hypochlorite.

For a wavelength window between 220 and 325 nm or a single wavelength at 290 nm if no interferences are present, the method can be applied for a concentration range of 0 to 400 mgClO⁻ L⁻¹ with a

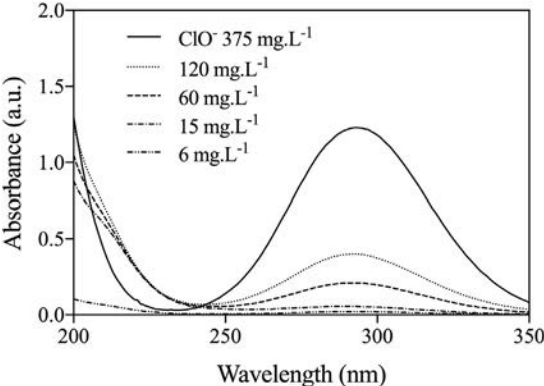


FIGURE 6.19 UV spectra of water (swimming pool and deodorization) containing hypochlorite.

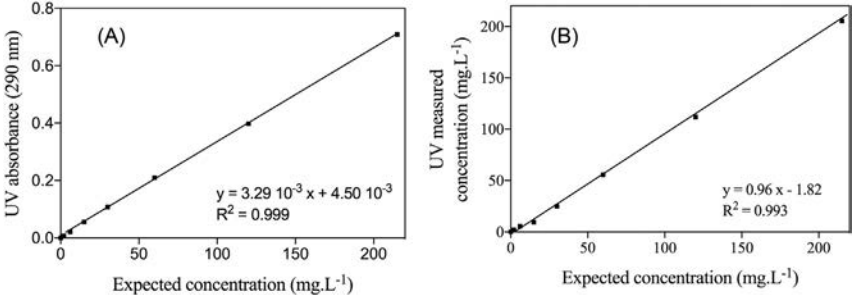


FIGURE 6.20 Hypochlorite detection by absorptiometry (A) or by semideterministic method (B).

detection limit of 5 mg L^{-1} . Using a 100-mm pathlength, this last can be lowered to 0.5 mg L^{-1} , a value acceptable for some regulation applications.

6.2.4.3 Organochlorine compounds

The use of UV spectrophotometry for the estimation of monochloramine in water distribution systems was recently reported [47], coupled with the determination of nitrate and nitrite. A model based on the absorbance values measured at 220, 245, 280, and 320 nm gave an estimate of monochloramine concentration. Implemented in an online UV–visible spectrophotometer, this method was applied to a given water distribution system and further experiments are needed to check the interest of the method on other sites, regarding potential interferences with organic matter and pH.

Finally, the monitoring of total organochlorine compounds (TOX) during chlorination was proposed from the decrease of the absorbance value at 272 nm [48]. This approach is detailed in Chapter 10.

6.3 Metallic constituents

The constant evolution of water quality standards implies the development of faster and cheaper analytical procedures. These are more particularly adapted for online measurement, for the frequent analysis of metallic constituents or for the estimation of global parameters. The cheapest and simplest methods for the determination of metallic constituents are colorimetric ones, which are less precise and selective than instrumental reference methods such as graphite furnace (GF)-AAS or ICP-OES. Other instrumental techniques based on electrochemical principles are also proposed for water quality monitoring, but they are relatively expensive, sensitive to interferences, and, thus, rather inappropriate for wastewater monitoring.

The improvement of UV–visible spectrophotometers has led to a renewal in the colorimetric procedures, actually absorptiometric, with the possibility of simultaneous metallic compound determination after selective complexation. Based on the reaction between a ligand and some metallic elements, these complexometric procedures use absorptiometry for final detection generally through flow analysis systems (CFA, FIA, or SIA).

Before considering some of these complexometric procedures with final UV–visible detection, designed for the simultaneous determination of metallic constituents, a more simple approach must be considered. In the case of UV–visible absorption for some metallic constituents without any reagent, it is interesting to check the feasibility of a direct absorptiometric

measurement. This is studied in the first part with the determination of chromium in water and wastewater.

6.3.1 Chromium (direct measurement)

6.3.1.1 Hexavalent chromium

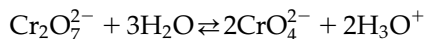
Chromium VI is one of the metallic contaminants often encountered in industrial wastewater, particularly for metal processing activities such as electroplating, for example. Because of its toxicity, its maximum concentration allowed in treated wastewater must generally be $50 \mu\text{g L}^{-1}$ before being discharged into a receiving medium.

There exist several analytical methods for chromium VI determination, often very complex [49,50]. One of the most simple and widespread methods is the former diphenylcarbazide colorimetric one. Its detection limit is about $1 \mu\text{g L}^{-1}$, but the procedure is time-consuming.

Another type of method is based on the spectrophotometric properties of Cr (VI), sometimes used as standard solution [51]. Moreover, the spectrophotometric determination of Cr (VI) is well known in the field of water examination, as it can be used for alternative measurement of chemical oxygen demand (COD) [52] (see Chapter 5). Two other UV–visible spectrophotometric methods have been proposed. The first one [53], designed for natural water, uses the peak height measurement at 372 nm, for a basified sample ($\text{pH} > 9$). The peak height is calculated from the absorbance values at three wavelengths (310, 372, and 480 nm), taking into account a very simple third-degree polynomial interference signal.

The second UV–visible spectrophotometric method [22] was proposed for natural and urban wastewaters with a more general mathematical compensation of interferences. Both UV–visible spectrophotometric methods are rapid and simple with a detection limit of around $5 \mu\text{g L}^{-1}$ for a 50-mm optical pathlength. Unfortunately, they cannot be applied for industrial wastewater survey, as the presence of specific compounds cannot be modeled by the mathematical tools used for the removal of interferences.

The application of the semideterministic approach, described in Chapter 3 and applied before in this chapter, can be used for the determination of hexavalent chromium. Exceptionally, the optical pathlength is 50 mm for this application because of the regulation compliance constraint. Contrary to the previous determination (nitrate, sulfide, hypochlorite, etc.), this application must take into account the pK_a value (about 5.8) of the dichromate in equilibrium with the chromate form:



As the pH of industrial wastewater must be around the pKa value (before neutralization), both chromate and dichromate spectra must be chosen in the basis of reference spectra, taking into account the influence of pH on chromium VI speciation (Fig. 6.21). The two first reference spectra correspond to chromium VI solutions of pH 3.5 and 9.5, respectively.

Fig. 6.22 shows real spectra from industrial wastewater and natural sample containing hexavalent chromium at different concentrations.

The spectra of Fig. 6.21 show two absorption peaks in the UV region, depending on pH, and a slight residual absorbance in the visible one. Bathochromic and hyperchromic effects can be noticed between the

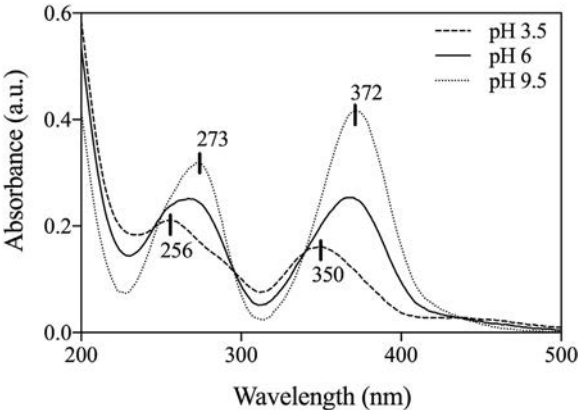


FIGURE 6.21 Absorption spectra of a $K_2Cr_2O_7$ solution (1 mg L⁻¹ of Cr, pathlength 50 mm) for different pH.

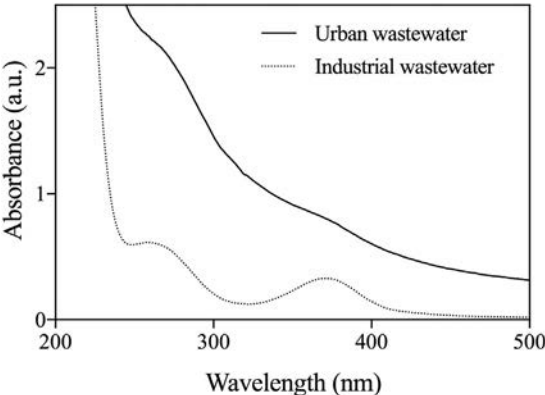


FIGURE 6.22 UV-visible spectra of wastewater containing hexavalent chromium.

acidic and basic media. The resulting visible color in the sample containing hexavalent chromium for neutral pH is orange.

A comparison between the diphenylcarbazide and UV–visible method for Cr (VI) determination was carried out for more than 50 samples of different origins (44 industrial wastewaters, 8 urban wastewaters, and 4 natural waters), the concentration of which varied between 0 and almost 1 mg L^{-1} . Fig. 6.22 shows some examples of the sample spectra. The results of the comparison are shown in Fig. 6.23, and the adjustment is quite good. For a wavelengths window between 300 and 450 nm, the method can be applied for a concentration range of 5 to $1000 \text{ } \mu\text{gCr L}^{-1}$ with a detection limit of $5 \text{ } \mu\text{g L}^{-1}$.

As the method is designed for industrial applications, the interference of some metallic compounds must be checked. Indeed, different ions, such as copper (II), iron (III), lead (II), and mercury (II), for example, potentially existing in electroplating wastewater, may interfere with the determination of Cr (VI). Except in the presence of Fe^{3+} , the measurement of Cr (VI) gives an error generally lower than 3% for 0.5 mg L^{-1} of metallic ion, and for greater concentrations (up to 10 mg L^{-1}), the error is negligible for Cu^{2+} , and lower than 15% for the other ions [54].

The reason why Fe^{3+} interferes is shown in Fig. 6.24. Even for a concentration of 1 mg L^{-1} , Fe^{3+} , which is the most probable form of dissolved iron in water which absorbs around 300 nm in acidic medium. In this case, the quadratic error of the deconvolution is too high. An increase of the pH value up to 9 (with some drops of NaOH 1M, for example) leads to the precipitation of the hydroxide form, the spectrum of which is very close to the reference of suspended solids. With this simple pretreatment, the error in Cr (VI) determination between the diphenylcarbazide and the UV–visible methods becomes lower than 2.5%.

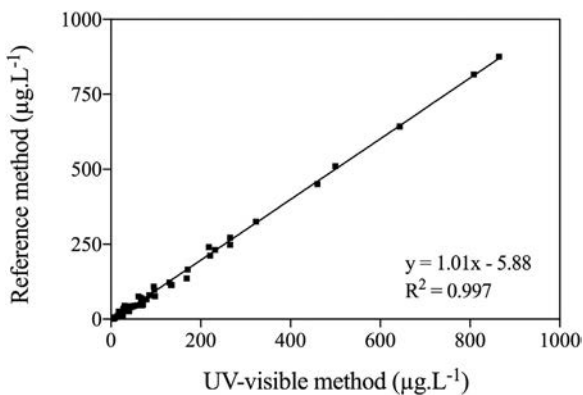


FIGURE 6.23 Comparison of the diphenylcarbazide and UV–visible method for Cr (VI) determination, for water and wastewater samples (pathlength 50 mm).

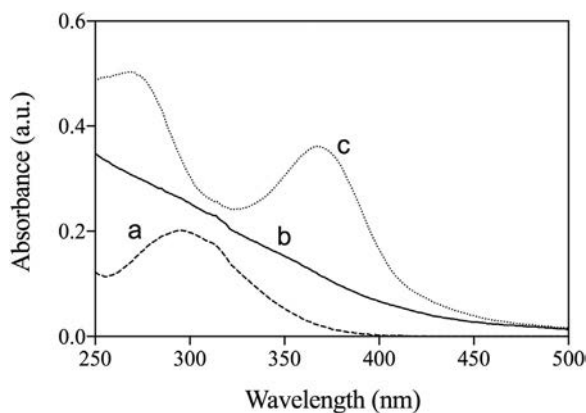


FIGURE 6.24 Absorption spectra (pathlength 50 mm) of synthetic solutions containing 1 mg L^{-1} of iron [a—pH 3, b—pH 9, and c—pH 9 and addition of Cr (VI)].

6.3.1.2 Trivalent chromium

Trivalent chromium (Cr^{3+} ion) is not as toxic as the hexavalent form and can be directly detected by visible spectrophotometry, its UV absorption being nonspecific. The UV–visible spectra of the trivalent form shows a great difference with the one of the hexavalent forms. At pH 1 and 5, two peaks of absorbance are noted at 433 and 600 nm, with very close absorbance values and giving a green color to the solution.

The main application of the optical properties of Cr^{3+} ion is the final colorimetric determination of COD with the measurement of absorbance at 600 nm, maximum of absorbance in acidic medium (see Chapter 5). As a consequence, the direct spectrophotometric determination of Cr^{3+} ion in water and wastewater is limited to highly concentrated samples.

Some methods for the indirect determination of Cr^{3+} ion in water or wastewater are proposed in the following section.

6.3.2 Metallic constituents determination by complexometry

Several procedures for the simultaneous determination of metallic constituents have been proposed at least for 25 years (Table 6.6). These analytical methods published since the 1990s show the evolution of the nature of the reagents and the spectrophotometric detection method. The majority of methods was implemented in flow analysis systems (CFA, FIA, or SIA), but the lack of substantial validation on real samples explains why these methods are actually not used for water or wastewater monitoring, for which reference methods such as ICP-OES are preferred.

TABLE 6.6 Complexometric procedures for the determination of metallic constituents.

Metallic constituents	Complexant/ reagent	Exploitation method	References
Ca, Mg	PAR	Multicomponent analysis	[52]
Cu, Co	MEDTA 5-BSAT	Derivative spectrophotometry PLS	[53,55]
Cd, Co, Cu, Pb, Mn, Ni, Zn	PAR	Multiple linear regression	[56]
Hg	Dithizone	Peak valley (480–585 nm)	[57]
Hg	Specific chemosensor	460 nm	[58]
Co, Cu, Pb, Mn, Ni, Zn, Fe	PAR	First-, second-, and third-derivative spectrophotometry	[59]
Cu, Fe	Bathocuproin/ LLE	Second-derivative spectrophotometry	[60]
Cr, Cu	MEDTA	Derivative spectrophotometry	[61]
Cu, Pd	Oxazolidine	Spectrum and first-order derivative spectrophotometry	[62]
Fe, Ag, Mn	Rhodamin B	Kalman filter	[63]
Ni, Co, Cu, Fe	PAR	Derivative spectrophotometry	[64]
Fe, Ru	Diphenyl phenantholin	Second-derivative spectrophotometry	[65]
Cu, Fe, Hg	Dithizon, EDTA, BHA	Deconvolution	[66]
Cu, Zn	Zincon	PLS	[67]
Cu, Ni, Co, Zn	Zincon Nitroso-R salt	PLS Kalman filter	[68,69]
Al, Fe	Hematoxylin Chrome Azurol/ SPE	PLS Measurement at 620 nm	[70,71]
U, Th, Zr	Arseno III/SPE	PLS	[72]
Zn, Cd, Pb	TAR	PLS	[73]
Cd, Zn, Co	Br-PADAP	PLS	[74]
Pb, Cu, Ni	MEDTA	Multiwavelength and derivative measurement	[75]

(Continued)

TABLE 6.6 (Continued)

Metallic constituents	Complexant/reagent	Exploitation method	References
Cu, Pd	Mesoporous adsorbent	Measurement at 425 (Cu) and 407 nm (Pd)	[76]
Fe	2,4,6-tripyridyl-s-triazine	Led spectrophotometer (600 nm)	[77]
Se	Composite adsorbent	Measurement at 430 nm	[78]
Cu, Ni, Co	SPE	PLS	[79]
Co	Composite adsorbent	Measurement at 420 nm	[80]
Ni, Mn, Zn, Ag, Cd, Fe, Hg, Cu, Sn, Co, Pb	Thiols, urease, bromothymol blue	Linear discriminant analysis	[81]

LLE, liquid–liquid extraction; *PLS*, partial least squares; *SPE*, solid-phase extraction.

All methods are based on the main complexometric reaction between a reagent (ligand) and some metallic elements, after a liquid–liquid or solid-phase extraction step if needed, and the resulting signal is exploited in order to determine the corresponding concentrations. The exploitation methods are different according to the methods, based on simple absorptiometry, derivative spectrophotometry, spectral deconvolution, or chemometrics methods (namely PLS). The choice of the different reagents (complexant, buffer, etc.) is obviously dependant on the metallic ion to be determined, but also on their optical properties (principally in the visible region). Several complexant mixtures are proposed in Table 6.6.

Concerning the choice of the metallic constituents, the majority of studies deal with the main metallic contaminants in water and wastewater, but some other elements found at ultratrace level are also considered (e.g., Co, Pd, and Ru).

As an example, a complexometric method for the simultaneous determination of Cu, Fe, and Hg in water and wastewater is presented more in details [66]. The complexant solution is based on the use of dithizone (diphenyl-1,5-thiocarbazone) widely used for metal analysis up to the seventies [82,83]. The dithizone solution is mixed with EDTA employed as masking agent, BHA (butylhydroxyanisol), glycine, ethanol, and distilled water.

Taking into account the possible metallic hydroxide precipitation and the potential presence of natural complexes (with humic substances in

natural waters, or with specific compounds in industrial wastewater) [84], the working pH is fixed at about 2.8, with a glycine solution for the stabilization of the dithizone spectrum. Notice that the glycine and its eventual metallic complexes are almost transparent in the UV region and do not change the general shape of the spectra of the final mixture [85]. Similarly, EDTA (in all the wavelength range) and BHA (transparent above 310 nm), alone or complexed, do not interfere with the UV signal except for copper and iron complexes, responsible for a great absorbance in the UV region.

The quantification of the metallic constituents studied [Cu (II), Hg (II), and Fe (II)] is carried out by the spectral semideterministic method or by any multicomponent procedure (see Chapter 3). The choice of the wavelength range depends on the studied element and on the corresponding basis of reference spectra. Moreover, the optical pathlength is either 10 or 50 mm for high or low concentration, respectively, with two reactive solution concentrations [85].

The UV–visible spectra of the metallic complexes constitute the basis of reference spectra used for the calculation of Cu (II), Hg (II), and Fe (II) concentrations. Fig. 6.25 shows these reference spectra (completed by a blank of the reagent) and also shows that the UV region is of poor interest for the purpose, taking into account the optical properties of the chosen reagents. Each of these spectra corresponds to a given concentration of a metallic constituent, which serve for the final concentration calculation of a sample. This value is dependant on several parameters, among which the concentration of the studied metal, related to the stoichiometric equilibrium (with dithizone) and the dilution rate of the

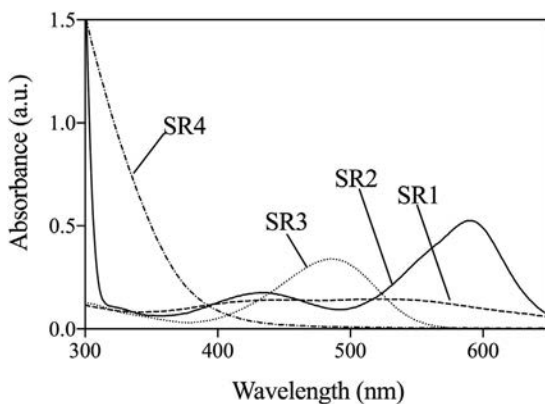


FIGURE 6.25 Reference spectra basis for the computation of Cu (II), Hg (II), and Fe (II) concentrations for the high-concentration mixture (10 mm cell pathlength) (SR1: Cu (II)-dithizonate, SR2: blank of the reagent, SR3: Hg (II)-dithizonate, and SR4: Fe (II)-EDTA complex) [54].

sample in the sample–reagent mixture. The metallic constituent concentration of an unknown sample corresponds to the product of this value by the contribution coefficient related to the corresponding dithizonate spectrum in the linear combination.

For natural waters and/or effluent applications, some interference may occur with the presence of natural or anthropogenic chelating agents. For example, humic substances can compete with dithizone for metallic constituent complexation in natural waters [86]. In this case, the degradation of organometallic complexes must be effective before the analytical determination. A photodegradation step, with a simple device as the one already proposed in this chapter for the determination of N and P compounds, can be used for the purpose. However, contrary to the previous procedure using an oxidative reagent, the decomplexation can be carried out without the reagent [73].

The characteristics of the method for high- and low-concentration mixtures are presented in Table 6.7. The precision values are calculated for the middle of their respective range, and the sensitivities correspond to the smallest concentration difference data that can be obtained, depending both on the spectrophotometer resolution (10^{-3} a.u.) and on the precision for the calculation of the contribution coefficient values. The detection limit values are three times the standard deviation of the blank.

Several experiments were carried out on samples of natural waters and industrial wastewaters (12 for Cu, 9 for Hg, and 14 for Fe), with standard additions for some samples [56]. The analysis of the samples was performed both by a reference method (GF-AAS for copper and iron, cold vapor-AAS for Hg) and by the proposed spectrophotometric method.

Fig. 6.26 shows the comparison results between the two methods for each metallic constituent. The correlation coefficients of the related

TABLE 6.7 Characteristics of the proposed method.

	Wavelength (nm)	Working range ($\mu\text{g.L}^{-1}$)	Detection limit ($\mu\text{g.L}^{-1}$)	Precision (%)
<i>Copper</i>	300–650	0–30	3	3.0
		0–600	100	5.6
<i>Mercury</i>	300–650	0–100	2	3.2
		0–5000	80	5.0
<i>Iron</i>	300–650	0–1500	45	0.5
		0–12,500	1200	0.4

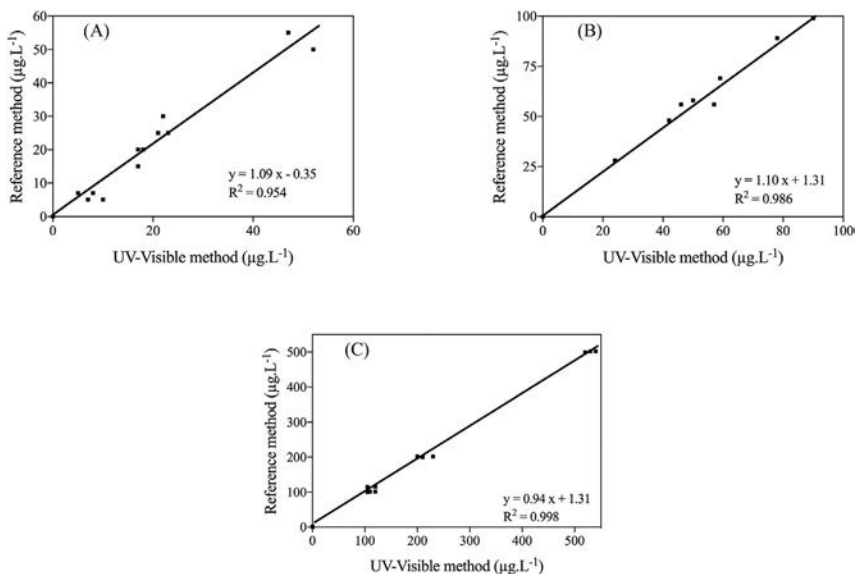


FIGURE 6.26 Comparison between the UV–visible spectrophotometric method and the corresponding reference methods for (A) copper, (B) mercury, and (C) iron determination, with or without standard additions of metals in sample.

regression lines are satisfactory and greater than 0.95 for the three studied metallic constituents, and the intercept values are very small compared to the concentration ranges.

Finally, despite the interest of this spectrophotometric approach, performance analytical techniques, such as ICP-OES or ICP-MS depending on the matrix, described as standard methods [2], are more adapted for water and wastewater quality monitoring.

References

- [1] A.E.E.W. Rice, R.B. Baird, *Standard Methods for the Examination of Water and Wastewater*, APHA, AWWA, 2017.
- [2] J. Birkmann, C. Pasel, M. Luckas, D. Bathen, UV spectroscopic properties of principal inorganic ionic species in natural waters, *Water Practice and Technology* 13 (2018) 879–892. Available from: <https://doi.org/10.2166/wpt.2018.097>.
- [3] U. APHA, *Standard methods for the examination of water and wastewater vol. 4*, 2017.
- [4] A. Azmi, A.A. Azman, S. Ibrahim, M.A.M. Yunus, Techniques in advancing the capabilities of various nitrate detection methods: a review, *International Journal on Smart Sensing and Intelligent Systems* 10 (2017) 223–261. Available from: <https://doi.org/10.21307/ijssis-2017-210>.
- [5] P. Singh, M.K. Singh, Y.R. Beg, G.R. Nishad, A review on spectroscopic methods for determination of nitrite and nitrate in environmental samples, *Talanta* 191 (2019) 364–381. Available from: <https://doi.org/10.1016/j.talanta.2018.08.028>.

- [6] M.A.P. Mahmud, F. Ejeian, S. Azadi, M. Myers, B. Pejic, R. Abbassi, et al., Recent progress in sensing nitrate, nitrite, phosphate, and ammonium in aquatic environment, *Chemosphere* 259 (2020) 127492. Available from: <https://doi.org/10.1016/j.chemosphere.2020.127492>.
- [7] M. Trojanowicz, K. Kolaćńska, Recent advances in flow injection analysis, *Analyst* 141 (2016) 2085–2139. Available from: <https://doi.org/10.1039/c5an02522b>.
- [8] L.O.C. Šraj, M.I.G.S. Almeida, S.E. Swearer, S.D. Kolev, I.D. McKelvie, Analytical challenges and advantages of using flow-based methodologies for ammonia determination in estuarine and marine waters, *TrAC - Trends in Analytical Chemistry* 59 (2014) 83–92. Available from: <https://doi.org/10.1016/j.trac.2014.03.012>.
- [9] M.I.G.S. Almeida, J.M. Estela, M.A. Segundo, V. Cerd, A membraneless gas-diffusion unit - multisyringe flow injection spectrophotometric method for ammonium determination in untreated environmental samples, *Talanta* 84 (2011) 1244–1252. Available from: <https://doi.org/10.1016/j.talanta.2010.12.052>.
- [10] O.W., USEPA, METHOD 1683 Specific Oxygen Uptake Rate in Biosolids Draft January 2001 U. S. Environmental Protection Agency Office of Water Office of Science and Technology Engineering and Analysis Division (4303). Science and Technology, EPA-821-R-13, 2001.
- [11] B. Roig, C. Gonzalez, O. Thomas, Simple UV/UV-visible method for nitrogen and phosphorus measurement in wastewater, *Talanta* 50 (1999) 751–758. Available from: [https://doi.org/10.1016/S0039-9140\(99\)00203-9](https://doi.org/10.1016/S0039-9140(99)00203-9).
- [12] V. Simeon, V. Butorac, V. Tomišić, N. Kallay, Existence of two forms of nitrate ion in dilute aqueous solutions. Thermodynamic parameters of interconversion, *Physical Chemistry Chemical Physics* 5 (10) (2003) 2015–2019.
- [13] V. Gvozdić, V. Tomišić, V. Butorac, V. Simeon, Association of nitrate ion with metal cations in aqueous solution: a UV-vis spectrometric and factor-analytical study, *Croatia Chemica Acta* 82 (2009) 553–559.
- [14] R.R.R.C. Hoather, Oxidised nitrogen in waters and sewage effluents observed by ultra-violet spectrophotometry, *Analyst* 84 (1959) 548–551.
- [15] P.J. Rennie, A.M. Sumner, F.B. Basketter, Determination of nitrate in raw, potable and waste waters by ultraviolet spectrophotometry, *Analyst* 104 (1979) 837–845.
- [16] K.T.M. Blanley, Automatic continuous-flow determination of nitrate in raw and potable waters, rivers and sewage effluents by ultraviolet absorption spectrometry, *Analyst* 109 (1984) 1053–1056.
- [17] A.C. Edwards, P.S. Hooda, Y. Cook, Determination of nitrate in water containing dissolved organic carbon by ultraviolet spectroscopy, *International Journal of Environmental Analytical Chemistry* 80 (2001) 49–59. Available from: <https://doi.org/10.1080/03067310108044385>.
- [18] J. Simal, M. Asuncion, I. Iglesias, Second derivative ultraviolet spectroscopy and sulfamic acid method for determination of nitrates in water, *Journal of Association of Official Analytical Chemists* 68 (1985) 1–3.
- [19] W.G. Crumpton, T.M. Isenhardt, P.D. Mitchell, Nitrate and organic N analysis with 2nd-derivative spectroscopy, *Limnology and Oceanography* 37 (1992) 907–913.
- [20] M.A. Ferree, R.D. Shannon, Evaluation of a second derivative UV/visible spectroscopy technique for nitrate and total nitrogen analysis of wastewater samples, *Water Research* 35 (2001) 327–332. Available from: [https://doi.org/10.1016/S0043-1354\(00\)00222-0](https://doi.org/10.1016/S0043-1354(00)00222-0).
- [21] J. Causse, O. Thomas, A.V. Jung, M.F. Thomas, Direct DOC and nitrate determination in water using dual pathlength and second derivative UV spectrophotometry, *Water Research* 108 (2017) 312–319. Available from: <https://doi.org/10.1016/j.watres.2016.11.010>.
- [22] O. Thomas, S. Gallot, E. Naffrechoux, Ultraviolet multiwavelength absorptiometry (UVMA) for the examination of natural waters and wastewaters Part III. Determination of chromium VI, *Fresenius Journal of Analytical Chemistry* 338 (1990) 241–244.

- [23] O. Thomas, F. Theraulaz, M. Domeizel, C. Massiani, UV spectral deconvolution: a valuable tool for waste water quality determination, *Environmental Technology (United Kingdom)* 14 (1993) 1187–1192. Available from: <https://doi.org/10.1080/09593339309385397>.
- [24] M. Karlsson, B. Karlberg Bo, R.J.O. Olsson, Determination of nitrate in municipal waste water by UV spectroscopy, *Analytica Chimica Acta* 312 (1995) 107–113.
- [25] G. Langergraber, N. Fleischmann, F. Hofstädter, A multivariate calibration procedure for UV/VIS spectrometric quantification of organic matter and nitrate in wastewater, *Water Science and Technology* 47 (2003) 63–71. Available from: <https://doi.org/10.2166/wst.2003.0086>.
- [26] P.J. Worsfold, P. Monbet, A.D. Tappin, M.F. Fitzsimons, D.A. Stiles, I.D. McKelvie, Characterisation and quantification of organic phosphorus and organic nitrogen components in aquatic systems: a review, *Analytica Chimica Acta* 624 (2008) 37–58. Available from: <https://doi.org/10.1016/j.aca.2008.06.016>.
- [27] K. Lin, J. Pei, P. Li, J. Ma, Q. Li, D. Yuan, Simultaneous determination of total dissolved nitrogen and total dissolved phosphorus in natural waters with an on-line UV and thermal digestion, *Talanta* 185 (2018) 419–426. Available from: <https://doi.org/10.1016/j.talanta.2018.03.085>.
- [28] B. Roig, C. Gonzalez, O. Thomas, Measurement of dissolved total nitrogen in wastewater by UV photooxidation with peroxodisulphate, *Analytica Chimica Acta* 389 (1999) 267–274. Available from: [https://doi.org/10.1016/S0003-2670\(99\)00212-3](https://doi.org/10.1016/S0003-2670(99)00212-3).
- [29] B. Roig, F. Pouly, C. Gonzalez, O. Thomas, Alternative method for the measurement of ammonium nitrogen in wastewater, *Analytica Chimica Acta* 437 (2001) 145–149. Available from: [https://doi.org/10.1016/S0003-2670\(01\)00944-8](https://doi.org/10.1016/S0003-2670(01)00944-8).
- [30] R.W. Low, G.K. McEvoy, S.R. Matthews, Formation of nitrate and ammonium ions in titanium dioxide mediated photocatalytic degradation of organic compounds containing nitrogen atoms, *Environmental Science Technology* 25 (1991) 460–467.
- [31] J.H. Lowry, K. Mancy, A rapid automated system for the analysis of dissolved total organic nitrogen compounds in lake waters, *Water Research* 12 (1978) 471–475.
- [32] P. Worsfold, I. McKelvie, P. Monbet, Determination of phosphorus in natural waters: A historical review, *Analytica Chimica Acta* 918 (2016) 8–20. Available from: <https://doi.org/10.1016/j.aca.2016.02.047>.
- [33] Q. Du, H. Chen, L. Zhao, F. Yu, detection of phosphorus species in water: technology and strategies, *Analyst* 144 (2019) 7130–7148.
- [34] E.A. Nagul, I.D. McKelvie, S.D. Kolev, The use of on-line UV photoreduction in the flow analysis determination of dissolved reactive phosphate in natural waters, *Talanta* 133 (2015) 155–161. Available from: <https://doi.org/10.1016/j.talanta.2014.07.058>.
- [35] O. Thomas, F. Théraulaz, V. Cerdà, D. Constant, P. Quevauviller, Wastewater quality monitoring, *TrAC Trends in Analytical Chemistry* 16 (1997) 419–424. Available from: [https://doi.org/10.1016/S0165-9936\(97\)82859-2](https://doi.org/10.1016/S0165-9936(97)82859-2).
- [36] F. Pouly, E. Touraud, J.F. Buisson, O. Thomas, An alternative method for the measurement of mineral sulphide in wastewater, *Talanta* 50 (1999) 737–742. Available from: [https://doi.org/10.1016/S0039-9140\(99\)00201-5](https://doi.org/10.1016/S0039-9140(99)00201-5).
- [37] M. Bowden, D. Diamond, The determination of phosphorus in a microfluidic manifold demonstrating long-term reagent lifetime and chemical stability utilising a colorimetric method, *Sensors and Actuators, B: Chemical* 90 (2003) 170–174. Available from: [https://doi.org/10.1016/S0925-4005\(03\)00024-8](https://doi.org/10.1016/S0925-4005(03)00024-8).
- [38] D. Jolley, W. Maher, P. Cullen, Rapid method for separating and quantifying orthophosphate and polyphosphates: application to sewage samples, *Water Research* 32 (1998) 711–716. Available from: [https://doi.org/10.1016/S0043-1354\(97\)00237-6](https://doi.org/10.1016/S0043-1354(97)00237-6).
- [39] D. Connell, *Basic Concepts of Environmental Chemistry*, CRC Press, 2005.

- [40] N.S. Lawrence, J. Davis, R.G. Compton, Analytical strategies for the detection of sulfide: a review, *Talanta* 52 (2000) 771–784. Available from: [https://doi.org/10.1016/S0039-9140\(00\)00421-5](https://doi.org/10.1016/S0039-9140(00)00421-5).
- [41] L. Ferrer, M. Miró, J.M. Estela, V. Cerdà, Analytical methodologies for reliable sulfide determinations in aqueous matrices exploiting flow-based approaches, *TrAC - Trends in Analytical Chemistry* 26 (2007) 413–422. Available from: <https://doi.org/10.1016/j.trac.2007.01.014>.
- [42] E.A. Guenther, K.S. Johnson, K.H. Coale, Determination of total sulfide and iodide in natural water, Moss Landing, Marine. Laboratories, Moss Landing Analytical Chemistry 73 (2001) 3481–3487.
- [43] S. Dupraz, B. Ménez, F. Guyot, Fast determination of the main reduced sulfur species in aquatic systems by a direct and second-derivative spectrophotometric method, *Journal of Chemistry* 2019 (2019). Available from: <https://doi.org/10.1155/2019/1039487>.
- [44] G. Leng, Q. Hu, W.F. He, Z. Liu, W.J. Chen, W.B. Xu, et al., A simple field method for the determination of sulfite in natural waters: based on automated dispersive liquid-liquid microextraction coupled with ultraviolet-visible spectrophotometry, *Journal of Chromatography. A* 1584 (2019) 72–79. Available from: <https://doi.org/10.1016/j.chroma.2018.11.017>.
- [45] R.B. Baird, A.D. Eaton, E.W. Rice, L. Bridgewater, *Standard Methods for the Examination of Water and Wastewater: 4500 Sulfate*, American Public Health association, Washington DC, 2017.
- [46] J.K. Salem, M.A. Draz, Synthesis and application of silver nanorods for the colorimetric detection of sulfate in water, *Inorganic Chemistry Communications* 116 (2020) 107900. Available from: <https://doi.org/10.1016/j.inoche.2020.107900>.
- [47] W. Sung, Technical note: using UV-vis spectrophotometry to estimate nitrite plus nitrate and monochloramine, *Journal of American Water Works Association* 103 (2011) 97–103.
- [48] G.V. Korshin, C.W. Li, M.M. Benjamin, The decrease of UV absorbance as an indicator of TOX formation, *Water Research* 31 (1997) 946–949. Available from: [https://doi.org/10.1016/S0043-1354\(96\)00393-4](https://doi.org/10.1016/S0043-1354(96)00393-4).
- [49] V.M. Rao, Determination of chromium in natural waters: a review, *Journal of Scientific and Industrial Research* 41 (1982) 607–615.
- [50] W. Ahmad, A.S. Bashammakh, A.A. Al-Sibaai, H. Alwael, M.S. El-Shahawi, Trace determination of Cr(III) and Cr(VI) species in water samples via dispersive liquid-liquid microextraction and microvolume UV–Vis spectrometry. Thermodynamics, speciation study, *Journal of Molecular Liquids* 224 (2016) 1242–1248. Available from: <https://doi.org/10.1016/j.molliq.2016.10.106>.
- [51] C. Burgess, *Standard in Absorption Spectrometry*, Chapman et al., Londres, 1981.
- [52] O. Thomas, N. Mazas, La mesure de la demande chimique en oxygène dans les milieux faiblement pollués, *Analisis* 14 (1986) 300–302.
- [53] A. Oumedjbeur, O. Thomas, Rapid determination of chromium (6) in natural waters, *Analisis (France)* 17 (1989).
- [54] E. Gomez, J.M. Estela, V. Cerda, Simultaneous spectrophotometric determination of calcium and magnesium in water, *Analytica Chimica Acta* 249 (1991) 513–518. Available from: [https://doi.org/10.1016/S0003-2670\(00\)83027-5](https://doi.org/10.1016/S0003-2670(00)83027-5).
- [55] L.N. Tu, L.V. Tan, N.X. Chien, Simultaneous spectrophotometric determination of Cu (II) and Co(II) using 5-bromosalicylaldehyde thiosemicarbazone by PLS method, *Rasayan Journal of Chemistry* 11 (2) (2018) 850–856.
- [56] E. Gomez, J.M. Estela, V. Cerda, M. Blanco, Simultaneous spectrophotometric determination of metal ions with 4-(pyridyl-2-azo) resorcinol (PAR), *Fresenius' Journal of Analytical Chemistry* 342 (4–5) (1992) 318–321.

- [57] F. Théraulaz, O.P. Thomas, Complexometric determination of mercury (II) in waters by spectrophotometry of its dithizone complex, *Microchimica Acta* 113 (1994) 53–59.
- [58] D. González-Morales, A. Valencia, A. Díaz-Nuñez, M. Fuentes-Estrada, O. López-Santos, O. García-Beltrán, Development of a low-cost UV-Vis spectrophotometer and its application for the detection of mercuric ions assisted by chemosensors, *Sensors (Switzerland)* 20 (2020). Available from: <https://doi.org/10.3390/s20030906>.
- [59] E. Bobrowska-Grzesik, A.M. Grossman, Derivative spectrophotometry in the determination of metal ions with 4-(pyridyl-2-azo)resorcinol (PAR), *Analytical and Bioanalytical Chemistry* 354 (1996) 498–502.
- [60] M.I. Toral, P. Richter, C. Rodríguez, Simultaneous determination of copper and iron by second derivative spectrophotometry using mixtures of ligands, *Talanta* 45 (1997) 147–153. Available from: [https://doi.org/10.1016/S0039-9140\(97\)00113-6](https://doi.org/10.1016/S0039-9140(97)00113-6).
- [61] H. Seco-Lago, J. Perez-Iglesias, J.M. Fernandez-Solis, J.M. Castro-Romero, V. Gonzalez Rodriguez, Simultaneous determination of chromium (III) and copper (II) by using derivative spectrophotometry with MEDTA, *Fresenius Journal of Analytical Chemistry* 357 (1997) 464–466.
- [62] A.A.Y. El-Sayed, M.A. Abdel Rahem, A.A. Omran, Zero- and first-order derivative spectrophotometry for individual and simultaneous determinations of copper(II) and palladium(II) using an oxazolidine derivative as a new reagent, *Analytical Sciences* 14 (1998) 577–583. Available from: <https://doi.org/10.2116/analsci.14.577>.
- [63] Y.Z. Ye, H.Y. Mao, Y.H. Chen, Catalytic kinetic simultaneous determination of iron, silver and manganese with the Kalman filter by using flow injection analysis stopped-flow spectrophotometry, *Talanta* 45 (1998) 1123–1129. Available from: [https://doi.org/10.1016/S0039-9140\(97\)00235-X](https://doi.org/10.1016/S0039-9140(97)00235-X).
- [64] L.L. Kolomiets, L.A. Pilipenko, I.M. Zhmud, Application of derivative spectrophotometry to the selective determination of nickel, cobalt, copper and iron (III) with PAR in binary mixtures, *Journal of Analytical Chemistry* 54 (1999) 28–30.
- [65] M.I. Toral, P. Richter, A.E. Tapia, J. Hernández, Simultaneous determination of iron and ruthenium as ternary complexes by extractive second derivative spectrophotometry, *Talanta* 50 (1999) 183–191. Available from: [https://doi.org/10.1016/S0039-9140\(99\)00118-6](https://doi.org/10.1016/S0039-9140(99)00118-6).
- [66] B. Coulomb, F. Theraulaz, V. Cerda, O. Thomas, Fast and simultaneous complexometric determination of copper (II), iron (II) and mercury (II) in natural waters and effluents using a robust UV-visible spectral deconvolution, *Química Analítica* 18 (1999) 255–262.
- [67] J. Ghasemi, A. Niazi, R. Leardi, Genetic-algorithm-based wavelength selection in multicomponent spectrophotometric determination by PLS: application on copper and zinc mixture, *Talanta* 59 (2003) 311–317. Available from: [https://doi.org/10.1016/S0039-9140\(02\)00505-2](https://doi.org/10.1016/S0039-9140(02)00505-2).
- [68] J. Ghasemi, S. Ahmadi, K. Torkestani, Simultaneous determination of copper, nickel, cobalt and zinc using zincon as a metallochromic indicator with partial least squares, *Analytica Chimica Acta* 487 (2003) 181–188. Available from: [https://doi.org/10.1016/S0003-2670\(03\)00556-7](https://doi.org/10.1016/S0003-2670(03)00556-7).
- [69] F. Zhou, C. Li, H. Zhu, Y. Li, A novel method for simultaneous determination of zinc, nickel, cobalt and copper based on UV–vis spectrometry, *Optik* 182 (2019) 58–64. Available from: <https://doi.org/10.1016/j.ijleo.2018.12.159>.
- [70] M.D.A. Niazi, J. Zolgharnein, Simultaneous determination of aluminium and iron using spectrophotometric and orthogonal signal correction-Partial Least Squares in plant and water, *Annali di Chimica* 97 (2007) 1181–1190.
- [71] P. Vanloot, C. Branger, A. Margailan, C. Brach-Papa, J.L. Boudenne, B. Coulomb, On-line solid-phase extraction and multisyringe flow injection analysis of Al(III) and Fe(III) in drinking water, *Analytical and Bioanalytical Chemistry* 389 (2007) 1595–1602. Available from: <https://doi.org/10.1007/s00216-007-1538-y>.
- [72] J.B. Ghasemi, E. Zolfonoun, Simultaneous spectrophotometric determination of trace amounts of uranium, thorium, and zirconium using the partial least squares method after

- their preconcentration by α -benzoin oxime modified Amberlite XAD-2000 resin, *Talanta* 80 (2010) 1191–1197. Available from: <https://doi.org/10.1016/j.talanta.2009.09.007>.
- [73] J.B. Ghasemi, B. Hashemi, Surfactant-mediated complex formation for determination of traces amounts of zinc, cadmium, and lead with 4-(2-thiazolylazo) resorcinol and chemometric methods, *Environmental Monitoring and Assessment* 183 (2011) 57–63. Available from: <https://doi.org/10.1007/s10661-011-1905->.
- [74] D. Xu, W. Fan, H. Lv, Y. Liang, Y. Shan, G. Li, et al., Simultaneous determination of traces amounts of cadmium, zinc, and cobalt based on UV-Vis spectrometry combined with wavelength selection and partial least squares regression, *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy* 123 (2014) 430–435. Available from: <https://doi.org/10.1016/j.saa.2013.12.086>.
- [75] M. Fernández-Feal, J. Castro-Romero, J. Fernández-Solís, Simultaneous determination of Pb(II), Cu(II) and Ni(II) with MEDTA by ultraviolet and visible derivative spectrophotometry, *Chemical Science International Journal* 22 (2018) 1–8. Available from: <https://doi.org/10.9734/csji/2018/40983>.
- [76] M.R. Awual, I.M.M. Rahman, T. Yaita, M.A. Khaleque, M. Ferdows, PH dependent Cu(II) and Pd(II) ions detection and removal from aqueous media by an efficient mesoporous adsorbent, *Chemical Engineering Journal* 236 (2014) 100–109. Available from: <https://doi.org/10.1016/j.cej.2013.09.083>.
- [77] B.J. Place, Activity analysis of iron in water using a simple LED spectrophotometer, *Journal of Chemical Education* 96 (2019) 714–719. Available from: <https://doi.org/10.1021/acs.jchemed.8b00515>.
- [78] M.R. Awual, T. Yaita, S. Suzuki, H. Shiwaku, Ultimate selenium(IV) monitoring and removal from water using a new class of organic ligand based composite adsorbent, *Journal of Hazardous Materials* 291 (2015) 111–119. Available from: <https://doi.org/10.1016/j.jhazmat.2015.02.066>.
- [79] Y. Guo, H. Zhao, Y. Han, X. Liu, S. Guan, Q. Zhang, et al., Simultaneous spectrophotometric determination of trace copper, nickel, and cobalt ions in water samples using solid phase extraction coupled with partial least squares approaches, *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy* 173 (2017) 532–536. Available from: <https://doi.org/10.1016/j.saa.2016.10.003>.
- [80] M.R. Awual, M.M. Hasan, A. Islam, A.M. Asiri, M.M. Rahman, Optimization of an innovative composited material for effective monitoring and removal of cobalt(II) from wastewater, *Journal of Molecular Liquids* 298 (2020) 112035. Available from: <https://doi.org/10.1016/j.molliq.2019.112035>.
- [81] W. He, L. Luo, Q. Liu, Z. Chen, Colorimetric sensor array for discrimination of heavy metal ions in aqueous solution based on three kinds of thiols as receptors, *Analytical Chemistry* 90 (2018) 4770–4775. Available from: <https://doi.org/10.1021/acs.analchem.8b00076>.
- [82] M.S.B.A. Budesinsky, Stability constants of some metal dithizonates, *Talanta* 20 (1973) 228–232.
- [83] H. Irving, G. Iwantscheff, The analytical application of dithizone, *Critical Reviews in Analytical Chemistry* 8 (1980) 321–366.
- [84] S.R.J.W. Moore, *Heavy Metals in Natural Waters*, Springer Verlag, New York, Berlin, Heidelberg, Tokyo, 1984.
- [85] F. Theraulaz, *Méthodes Complexométriques Rapides de Dosage Des Métaux Dans Les Eaux Par Spectrophotométrie UV-Visible*, de Savoie, Chambéry, France, 1993.
- [86] J. Buffle, *Complexation Reactions in Aquatic Systems: An Analytical Approach*, Ellis Horwood Limited, Chichester, 1988.