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CYANIDES CONCENTRATION AND SPECTROPHOTOMETRIC DETERMINATION, MEETING THE TIGHTEN REQUIREMENTS FOR SURFACE WATER MONITORING

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ABSTRACT. Tightened requirements for surface water monitoring pose in front of small laboratories challenges related to determination of cyanides concentrations. A reliable simple method for cyanides preconcentration in real water samples, preserved by addition of NaOH to pH 12.0-12.5, is proposed. The optimum conditions found are: water samples evaporation, as alkalised, at 70 °C, while being stirred or without stirring, for up to one hour to achieve 2.5-3.5 fold concentration of the sample. The cooled preconcentrated samples, can be analysed using Spectroquant® 1.09701 Cyanide Test, which corresponds to DIN 38405-13 and is analogous to ISO 6703, EPA 335.2, APHA 4500-CN-E, and ASTM D2036-09 D. Concentrations in the range of 0.001 – 0.005 mg/L free CN^- can be determined with satisfying accuracy and reproducibility.

Keywords: cyanides, surface water, spectrophotometry, monitoring, ion exchange,

КОНЦЕНТРИРАНЕ И СПЕКТРОФОТОМЕТРИЧНО ОПРЕДЕЛЯНЕ НА ЦИАНИДИ, ОТГОВАРЯЩО НА ПОВИШЕНИТЕ ИЗИСКВАНИЯ ЗА МОНИТОРИНГ НА ПОВЪРХНОСТНИ ВОДИ

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РЕЗЮМЕ. Повишените изисквания към мониторинга на повърхностните води поставят пред малките лаборатории предизвикателства, свързани с определяне на цианиди в ниски концентрации. В работата се предлага надежден и прост метод за предварително концентриране на цианиди в реални водни проби, консервирани чрез добавяне на NaOH до pH 12.0-12.5. Оптималните определени условия са: изпаряване на водните проби, както са алкализирани, при 70 °C, при разбъркване или без разбъркване, в продължение на един час, за да се постигне 2.5-3.5 кратно концентране на пробата. Охладените концентрирани проби, могат да бъдат анализирани, като се използва Spectroquant® 1.09701 тест за цианиди, който съответства на DIN 38405-13 и е аналогичен на ISO 6703, EPA 335.2, APHA 4500-CN-E и ASTM D2036-09 D. Концентрации в обхвата 0.001 - 0.005 мг / л свободни CN^- може да се определят с удовлетворяваща точност и възпроизводимост.

Ключови думи: цианиди, повърхностни води, спектрометрия, мониторинг, йонен обмен

Introduction

Cyanides enter the environment from natural and anthropogenic sources. Industrial wastes are the most important sources. Cyanides are used in electroplating, plastics and pharmaceutical production, metallurgy, mining activities, etc. Various industries worldwide produce around 1400000 tons of cyanide per year (Rosentreter et al., 2015). Under normal conditions, the concentrations of hydrogen cyanide (HCN) and cyanide ion (CN^-) are equal at pH of approximately 9.4. At lower pH value the amount of HCN increases reaching practically over 99 % at pH < 7, and at pH >11 practically only CN^- are available in the water (over 99 %) (Scott and Ingles, 1981). The sum of HCN and CN^- in a sample is refefred to as "free cyanide". For analytical purposes "free cyanide" is defined as the amount of HCN liberated from a solution at pH 6.0. Metal cyanide complexes (of Zn, Cd, Cu, Hg, Ni, and Ag) that dissociate under weak acid conditions of pH 4.5 – 6.0 to produce environmentally significant concentrations of free cyanide are refefred to as "weak acid dissociable" (WAD) cyanide. Complexes of cyanide with gold, cobalt and iron are strong and stable, in solution they degrade much more slowly than WAD cyanide under normal chemical and physical conditions and are reffered to as "strong cyanide complexes".

"Free cyanide" is bioavailable and toxic to mammals and to organisms in aquatic environments. Cyanide's toxicity results from its tendency to bind irreversibly to the iron of the enzyme cytochrome C oxidase, hindring the electron transport from cytochrome C oxidase to oxygen and resulting in hypoxia. Tissues that mainly depend on aerobic respiration, such as the central nervous system and the heart, are mainly affected. The "dose–effect" curve of the acute effects of HCN and CN^- in humans is steep. While slight effects occur at exposure to HCN levels of 20–40 mg/m^3, 50–60 mg/m^3 can be tolerated for 20 min to 1 h without immediate or late effects, 120–150 mg/m^3 are dangerous to life and may lead to death after 0.5–1 h, 150 mg/m^3 dose is likely to be fatal within 30 min, 200 mg/m^3 is likely to be fatal after 10 min, and 300 mg/m^3 is immediately fatal. Acute exposure to cyanide has occurred most frequently by the oral route from suicides or by accidental poisonings. It was estimated that death occurred after absorption of an average of 1.4 mg CN^-/kg body weight. The lowest determined fatal dose is 0.54 mg CN^-/kg body weight. In most poisoning cases, a large amount of the ingested cyanide remained in the gastrointestinal tract (thus, using the dose ingested as an indicator of the lethality of cyanide is misleading) (UNEP, 2004). Acute toxicity concentrations to various fish species is in the range of 20-640 µg CN^- per liter. The more sensitive rainbow and brown trout generally exhibit acute toxicity in the range of 20-80 µg/L of free cyanide. Chronic toxic effects are reported in fish in the range of 5-20 µg/L. Cyanide concentrations that kill fish often do not adversely impact lower aquatic organisms like crustaceans and mussels (Ingles and Scott, 1987). The highest concentration of cyanide allowed in drinking water by the US EPA (Environmental Protection Agency) is 200 µg/L (EPA, 1983). The Directive 1998/83 of the European Parliament on the quality of drinking water sets lower limit of 50 µg/L (EU, 1998), while the maximum amount of cyanides allowed in mineral waters according to Directive 2003/40/EU is 70 µg/L (EU, 2003), which is the same as the World Health Organization limit in drinking water (WHO, 2008). For preserving ecosystems lower limits are needed and that's why Australian and New Zealand Environmental and Conservation Council set a standard of trigger values for freshwater and marine water (that provides for protection of 99% of the species) as 4 and 2 µg/L, respectively (ANZECC, 2000).

Bulgarian legislative documents (Decree № 9 / 2001 for the quality of water intended for drinking purposes, Decree № 12 / 2002 on quality requirements for surface water intended for drinking water supply and Decree 1 / 2007 for exploration, use and protection of groundwater) introduced 50 µg/L as a maximum allowable concentration of cyanides (Bulgarian Council of Ministers, 2001; Bulgarian Council of Ministers, 2002; Bulgarian Council of Ministers, 2007). Decree N-4 on the surface waters characterization (Bulgarian Council of Ministers, 2013) gives as the maximum allowable concentration of 5 µg/L free cyanide (CN-), however, the regulated average annual value should be 1 µg/L free cyanide. To check the compliance to such standards is demanding work.

Methods for free cyanides determination

The aquatic "free cyanide" analytical method reports the sum of both forms of free cyanide – the cyanide ion (CN^-) and hydrogen cyanide (HCN), plus cyanide from the breakdown of the weak complexes that dissociate into free cyanide at pH 6 to pH 8 in an aquatic environment. Methods applied to determine "free cyanide" concentrations should not alter the stability of stronger cyanide complexes, as they may otherwise be included in the free cyanide result.

Optical methods

Titrimetric determination of cyanides is based on the development of turbidity due to silver cyanide that forms as a result of the reaction between the cyanide and added silver nitrate solution. Various modifications to the argentometric procedure have been suggested.

Spectrophotometric methods for cyanide assessment are based on direct, indirect and enzymatic reactions. Conversion of cyanide into cyanogen chloride or cyanogen bromide followed by chromogenic reactions with pyridine solutions of barbituric acid or isonicotinic acid-barbiturates have been suggested for use in static mode for determining cyanide over the concentration range 0.04–1.20 µg/mL with a detection limit of 0.02 µg/mL and for hydrodynamic analysis of 0.4–5.2 µg/mL cyanide (Hassanet al., 2007). Direct reaction of cyanide with 2,2-dihydroxy-1,3-indanedione in alkaline media (Drochioiu, 2002) or ninhydrine to give colored products has been reported (Chueachot and Chantal, 2014). Enzymatic spectrophotometric determination of cyanide involves catalytic oxidation of l-tyrosine using tyrosinase enzyme. The dark colour, developed due to the formation of melanin, is suppressed by cyanide ion (Tatsuma et al., 2000).

Determination of cyanide by indirect methods is based on decoloration of some colored complexes such as Ag^+/*N*-(2-thiozolyl-2-hydroxybenzamide) (Garg et al., 1999), Cu^{2+}/*N*,*N*-diethyl-1,4-phenylene-diamine (Hoshino et al., 2003). Determination of cyanide in drinking and ground waters is described, which is based on its catalytic effect on the oxidation of Janus green (and decrease in its absorbance). The method can be applied in the range of 0.01 – 0.5 mg/L CN^- with a detection limit of 0.007 mg/L (Abbasi et al., 2010). Reaction of cyanide ions with a chlorinating agent to form cyanogen chloride, which in turn reacts with 1,3-dimethylbarbituric acid to form a violet dye (pyridine-free König reaction), which is determined photometrically, is the basis of Spectroquant® 1.09701 Cyanide Test, which is widely accepted. The method corresponds to DIN 38405-13 and is analogous to ISO 6703, EPA 335.2, APHA 4500-CN- E, and ASTM D2036-09 D. The method can be used in the range of 0.002 – 0.5 mg/L CN^-. Many cyanine dyes are both colored and fluorescent. Shang and Dong (2009) have described a way of measuring cyanide, based on the fact that in an oxygen-bearing solution (air exposure), cyanide forms aurocyanide complex. Fluorescence is observed when a fluorescent dye and gold nanoparticles present in the same solution under "tuned conditions". When cyanide is added to this solution, it rapidly attacks the gold nanoparticles, reducing their size and the observed fluorescence emission changes. A limit of detection (LOD) of 0.6 µM was reported. The fluorescence of CdTe quantum dots (QDs) is significantly reduced by the presence of small amounts of Cu^{2+} ions which adsorb on the CdTe QDs and the paramagnetic Cu^{2+} quenches the fluorescence. In the presence of cyanide, the fluorescence is restored as CN^- complexes the Cu^{2+} and removes it from the QDs surface. The LOD of 0.15 µM is reported (Shang et al., 2009). A fluorescence method is described for selective and sensitive determination of cyanide ion in aqueous solution based on functionalized zinc sulfide (ZnS) quantum dot as luminescent prob. The ultra-small ZnS nanoparticles exhibited a strong fluorescent emission at about 424 nm. The fluorescence quenching is observed in presence of CN^- ions, which interact with ZnS QDs. The method can be applied in the range 2.44×10^{-6} to 2.59×10^{-5} M CN^- with a detection limit of 1.70×10^{-7} M at pH 11 (Shamsipur and Rajabi, 2014). Gavrilov et al. (2005) reported a method based on the enhanced chemiluminescence of alkaline solutions of luminol, containing p-nitrobenzaldehyde and hemin, in presence of cyanide. They claimed a LOD of $\cong$4 nM.

Electrochemical methods

The cyanide titration with $AgNO_3$ with potentiometric endpoint determination was first reported in 1922. The most widely used indicator electrode is the silver rod. Two points of inflexion are obtained in the potentiometric titration curve, the first being due to the formation of a soluble silver complex, and the second is related to the appearance of insoluble silver(I) cyanide:

$$Ag^+ + 2CN^- \rightarrow [Ag(CN)_2]^-$$

$$Ag^+ + [Ag(CN)_2]^- \rightarrow Ag[Ag(CN)_2].$$

The change in slope of the first potentiometric inflexion is about ten times greater than that of the second and it is less susceptible to interferences. That's why, it is normally used in practical applications.

Commercial ISEs for cyanide are available, however, they display numerous interferences with halides, sulfide and various metals that are complexed by cyanide, e.g., cadmium, silver, zinc, copper, nickel and mercury (ATSDR, 2014).

Amperometric titrations are the choice for relatively low concentrations of cyanide and for automated procedures. For amperometric titrations, rotating or vibrating platinum electrodes are preferred, with dilute silver nitrate solution as the titrant. The developed electrode, made of silver nanoparticles doped silica nanocomposite on gold, uses the electrochemical reaction that occurs between the Ag nanoparticle and CN^-. The reported LOD is 14 nM (Taheriet al., 2009). The amperometric detection of CN^- is subjected to interferences and the electrode response changes over time. The electrode must be frequently reconditioned and recalibrated. The first is achieved by carrying out a chromatographic separation prior to amperometric detection. The second problem is avoided by rapidly cycling the electrode through pre-measurement, measurement and cleaning potentials. The two techniques together are referred to as ion chromatography with pulsed amperometric detection (IC–PAD) (Ma and Dasgupta, 2010). Christison and Rohrer (2007) stabilized cyanide by treating the sample with sodium hydroxide, then removed transition metals with a cation-exchange cartridge, and applied amperometric detection achieving a LOD less than 40 nM cyanide.

Modern instrumental analysis

The cyanide can be measured by indirect flame atomic absorption spectrometry (FAAS). Cadmium carbonate on silica gel bed was used and a LOD of 0.2 mg/L was achieved (Noroozifar et al., 2005). Dadfarnia et al. (2007) applied a micro-column of immobilized (N,N''-bis(salicylidene) ethylenediamine) on sodium dodecyl sulphate - coated alumina, saturated with silver ion. With dilute NaOH as carrier, they inject a 250 µL aliquot of the cyanide bearing sample. A detection limit of 0.06 mg/L cyanide was reported.

Mass spectrometry, gas chromatography-mass spectrometry, gas chromatography (GC) with nitrogen-phosphorus detector (NPD), and the electron capture (ECD) detectors have been developed and used mainly for determining the cyanide in biological samples (blood, plasma, urine). Their LOD is in the range of 0.57 - 3 µg/L (Themelis et al, 2009; Ma and Dasgupta, 2010). A gas chromatography–tandem mass spectrometric (GC–MS/MS) method has been established for the determination of cyanide in surface water. This method is based on the derivatization of cyanide with 2-(dimethylamino) ethanethiol in surface water. The organic derivative was extracted with 3 mL of ethyl acetate, and then measured by using GC–MS/MS. Under the established conditions, the detection and quantification limits were 0.02 µg/L and 0.07 µg/L. The common ions Cl^-, F^-, Br^-, NO_3^-, SO_4^{2-}, PO_4^{3-}, K^+, Na^+, NH_4^+, Ca^{2+}, Mg^{2+}, Ba^{2+}, Mn^{4+}, Mn^{2+}, Fe^{3+}, Fe^{2+} and sea water did not interfere in cyanide detection, even when present in 1000-fold excess over the CN^- species (Kang and Shin, 2014). Table 1 compares different analytical methods for determining cyanide in environmental water samples, on the basis of the data, available in the already cited papers.

Table 1. *Comparison of different analytical methods for determining cyanide in environmetal water*

Method	LOD, µg/L	Method	LOD, µg/L
Amperometry with novel electrodes	0.4	HPLC – FLD	0.1
Atomic absorption spectrometry	60	HPLC – UV	10
Chemilumines-cence	0.1	IC - PAD	1
FIA/ Spectrophotometry	20	ISE/Potentio-metry	50-650
FIA/FAAS	60	QCMM	2
Fluorimetry	15	QD Fluorimetry	0.4
GC – NPD, GC - ECD	0.6 - 3	Spectrophoto-metry	2
GC–MS/MS	0.02	Titrimetry	1000

FIA – Flow injection analysis, FAAS – Flame atomic absorption spectrometry, ISE – ion sensitive electrode, UV – spectrophotometric method, FLD – Fluoriscence detector, QCMM - Quartz crystal mass monitor

As it can be seen from the Table 1, the spectrophotometry – a method which can be used practically even in not highly equipped laboratory, gives good results in the low concentration range. If the sample can be concentrated 2- 4 times by simple methods, the spectrophotometry would be the suitable choice to monitor surface water in compliance with the latest stringent requirements for surface waters protection.

Methods for cyanides concentration

In general, some ions in a sample can be concentrated using: selective precipitation followed by dissolution; solvent extraction followed by stripping; ion exchange, followed by elution; and sample partial evaporation. Of course, in the latter case, the concentration of all ions presenting in the water is increased. Since the aim was to concentrate water bearing very low concentrations of CN^-, precipitation was not considered as suitable method.

Four cycles of cyanide extraction from water samples (500 mL) with 25 mL of 0.25 M tributyltin hydroxide in trichloroethylene, which is then stripped with 2 M sodium hydroxide, the organic reagent being used for a further extraction of the water sample, followed by titration with silver nitrate solution, with *p*-dimethyl-benzylidene-rhodanine as indicator, gave a LOD of 4 µg/L (Wronski, 1981). The method is labor intensive and uses a compound of the banned TBT (UNEP, 2009).

That's why the present work was aimed at studying ion exchange, followed by elution, and sample partial evaporation as means for cyanides concentration.

Cyanides preconcentration by the use of amine-functionalized anion-exchange resins, followed by back-extraction with a sodium hydroxide solution has been reported (Pohlandt et al., 1983; Kurama and Çatalsarik, 2000). It has been found that cyanide decomposition depends on the temperature and time. At initial CN^- concentration of 0.2 M (with pH of 13.3), the observed loss of cyanide was correspondingly 0.0 and 1.1 and 5.7 % - for 30 min at temperatures 50, 72 and 95 ^oC. For the same temperatures, but for 24 hs, the loss of cyanide was correspondingly 2.2, 20.2 and 84.5 %. The oxidation of cyanide is facilitated in the presence of oxygen in the cyanide-bearing solution (Adams, 1990). These findings directed us to the idea of working at 55 and 70 ^oC and of studying the impact of water stirring.

Methods and materials

Experiments were conducted with model waters, bearing 0.005 mg/L CN^-, prepared by spiking distilled water and three different types of table-water (Table 2) with 1 mg/L KCN solution (prepared by using 1 g/L KCN Merck Ref. No. H032.01.O.L1, 99.99% KCN and distilled water). Five liters of different matrixes model waters were prepared to be used in all experiments, and solutions pH was risen to 12.3 by adding sodium hydroxide, following the procedure used to preserve field real water samples. Chosen method for concentration was applied also to real surface and ground water samples.

The ion-exchange resin, Wofatit AD 41 was used. Experiments were conducted batch wise in a cylindrical glass column with a diameter of 10 mm and a height of 75 mm. The resin (10 g) was packed into the column above glass wool. 50 mL of cyanide bearing water was left to contact with the resin for 2 hours. Then, the elution was carried out in 3 stages, each one with 5 mL 0.2 M NaOH solution. (Volumes, contact time and concentrations used were determined by preliminary experiments, carried out with distilled water spiked with KCN solution.)

Table 2. *Macro-parameters of used table-water matrixes.*

Water type, Component	Type I	Type II	Type III
Na^+	20.0	84.21	28.00
K^+	3.1	0.57	0.40
Ca^{2+}	72.7	8.29	1.60
Mg^{2+}	7.8	1.10	3.5
Cl^-	7.7	11.66	2.84
SO_4^{2-}	69	107.2	19.75
HCO_3^-	231	78.08	15.25
CO_3^{2-}	-	8.40	27.01
pH	7.23	8.71	9.65
χ, μS/cm	550	420	140

Type I - Hydrogen carbonate-sulfate-calcium; Type II - Sulfate-hydrogencarbonate–sodium; Type III - Carbonate-sulfate-sodium

Evaporation experiments were conducted with 50 mL samples of different table waters, bearing cyanide. Impact of temperature, water pH value, treatment time, and sample stirring was studied. The impact of pH value was studied by carrying out experiments with CN^- - bearing water with initial pH values of 9.8 and 12.3. To reach a concentration coefficient (initial water volume to water volume after evaporation) in the range 2.5 – 3.5 was aimed. Temperature was kept with the aid of Huber MPC K6 thermostat, pH was measured with Hanna pH 211 and adjusted with H_2SO_4 (1:1), 2 M H_2SO_4, and 2 M NaOH. Concentration of cyanides was determined with Spectroquant Cyanide test kit and Spectroquant NOVA 60 spectrophotometer.

The relative error (Δ, %), standard deviation (σ) and the confidence limits (ξ) were calculated using the following equations:

$$\Delta, \% = (x_r - x_{av}) / x_r, \qquad (1)$$

where x_r – real value (0.005 mg/L CN^-), achieved by precise addition of known amount of standard solution of KCN; x_{av} – the average of all measured values;

$$\sigma = \{[\sum (x_i - x_{av})^2] / (n-1)\}^{1/2}, \qquad (2)$$

where, x_i – the corresponding measured value; x_{av} – as above; and n – number of measurements;

$$\xi = x_{av} \pm (t \, . \, \sigma) / n^{1/2}, \qquad (3)$$

where t – the Student's (T) distribution factor for two-sided critical regions, taken for 95 % statistical probability, n and x_{av} – as above.

Results and discussion

Ion-exchange experiments carried out with distilled water, polluted with CN^-, showed good accuracy and reproducibility of the method. However, when table-waters were used as CN^- carrier, the accuracy decreased and the determined concentrations were around 50 % of the theoretical one. These data could be explained by the fact in the presence of metal ions cyanides are known to act as a strong ligand forming stable complexes. It has been shown that organic anion exchanger has very high affinity towards some of the metal-cyanide complexes (Dainton, 1965). That is the reason why their elution becomes challenging procedure. It was established that using ion exchange resin (as well as other type of sorbents) to remove heavy metals (zinc, copper) from pure systems is very effective but in the presence of cyanide ions the resins capacity rapidly decreases (Bose, 2002). One must also take into consideration the fact that in "real" water the concentration of presenting anions - macro-components is a lot higher than the concentration of cyanide anions, so that those anions can affect the ion exchange process by competition for functional groups. Other major problem is that it is difficult to find resin which is selective towards cyanide anions. That contributes to the problem, especially when cyanides concentration is in ppb range (Fernando, 2002). That obstacle could be overcome by using reactive ion exchange method as some authors suggest. The process includes in situ precipitation of metal cyanides (in form of hexacyanoferrate (II) and (III)) thus allowing preconcentration of ppb range with a factor of 100 or more. However, the procedure requires significant time and efforts.

Data from experiments, carried out with three parallel samples of the each of the three types of CN^- - bearing water matrixes, at temperatures of 55 °C (at time of 3 hours) and 70 °C (at time of 1 hour), and initial pH value of 9.8, gave as result of the analysis, cyanide concentrations around 50 % of the theoretical one. Data from experiments, carried out under the same conditions, but at the initial pH of 12.0 gave as result of the analysis, cyanide concentrations in the range of 60 - 90 % (for 55 °C), and in the range of 92 - 102 % (for 70 °C), compared to the theoretical one. The conclusion drawn is that real water samples have to be concentrated in the state as received from the field sampling, i.e. preserved with NaOH till pH of 12 – 12.5.

Data from additional to above-described experiments, carried out with three parallel samples of the each of the three types of CN^- - bearing water matrixes, with initial pH value of 12.3, and different times - 3 hours (at 55 °C) and 1 hour (at 70 °C), gave as result of the analysis, cyanide concentration in the range of 65 - 93 % (for 55 °C), and in the range of 95 - 105 % (for 70 °C), compared to the theoretical one. Lower concentrations, especially for samples concentrated at 55 °C, were measured when types I and II of water matrixes were used. This could not be attributed to the impact of matrix water initial pH value on the cyanide speciation, since initially water pH was raised to 12.3 and then CN^- was added.

Since better results were obtained for shorter evaporation times at higher temperatures, further experiments were conducted under these conditions. Three parallel samples of the each of the three types of CN^- - bearing water matrixes, with pH 12.3 were heated for 40 min at 70 °C and mixing (300 rev/min, MR 25 stirrer, Germany). Results, obtained for cyanides concentrations were in the range of 95 - 105 %, compared to the theoretical one. Consequently, samples mixing for relatively short heating time at 70 °C did not lead to a decrease in the analytical results.

Ten parallel samples of the each of the three types of CN^- - bearing water matrixes were evaporated for 1 hour at temperature of 70 °C without mixing. A concentration coefficient in the range 2.5-3.5 was achieved, the difference is attributed mainly to the difference in thickness, diameter and glass type of the beakers used, as well as to small variations in heating time. In general, no significant differences in the determined cyanide concentrations were found for the upper and lower limit of the concentration coefficient range. Data obtained were used to calculate the accuracy and precision – Table 3.

The preconcentration method (evaporation for 1 hour at temperature of 70 °C) was used to analyze real samples of surface and groundwater, which were preserved by addition of NaOH to reach pH 12.4. Concentrations obtained were in the range of 0.001 – 0.004 mg/L CN^-. Good assay reproducibility was obtained, based on three determinations for each water sample.

Table 3. *Macro-parameters of used table-water matrixes.*

Water type, parameter	Δ, %	σ	ξ, mg/L
Type I	- 7,8	$2,589 . 10^{-6}$	0,0046±0,000002
Type II	- 6,6	$2,441 . 10^{-6}$	0,0047±0,000002
Type III	+ 7,8	$1,909 . 10^{-6}$	0,0054±0,000001
The three types together	- 2,2	$1,071 . 10^{-5}$	0,0047±0,000008

Conclusion

A reliable simple method for cyanides preconcentration in real water samples, preserved by addition of NaOH to pH 12.0-12.5, has been developed. Water samples have to be evaporated, as alkalized, at 70 °C for up to one hour to achieve 2.5-3.5 fold concentration of the sample. Samples stirring can decrease the heating time to 40 min. The preconcentrated samples, after being cooled, can be analyzed using Spectroquant® 1.09701 Cyanide Test, which corresponds to DIN 38405-13 and is analogous to ISO 6703, EPA 335.2, APHA 4500-CN- E, and ASTM D2036-09 D. This way determinations can be realized which meet the tighten requirements for surface waters characterization.

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