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New method for complete recovery of total cyanide in water and soil and its application at the Samira gold mine (Niger)

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Cyanide is a very toxic substance, which occurs in various forms in environmental matrices and its determination requires a good extraction method. From the reference method of cyanide distillation by reflux heating under acidic conditions and entrainment of HCN gas collected as CN⁻ ions with detection by UV-Visible spectrophotometry, an improved and complete procedure for total cyanide extraction in aqueous and solid matrices has been developed. The best conditions after optimization of complete recovery ($\approx 100\%$) of total cyanide and elimination of interferences in natural waters and soils fortified are: heating at 181.75°C, saving of reflux time to 30 min, sulfuric acid concentration of 0.6 M, 2 to 4 times less acid, without catalyst and other special treatments of interferences relatively to existing techniques. Application to water samples (drinking, surface, underground) and effluents collected at the Samira gold mine (Niger) and its environs shows the impact of distillation extraction on total cyanide recovery. Waters, exempt of cyanide at the starting of mining activity, currently contain total cyanide contents of 1 to 5 $\mu\text{g L}^{-1}$ and in effluents up to 37 times the discharge standard (1 mg L^{-1}).

Key words: Cyanide decomposition, distillation extraction, environmental matrices, Samira gold mine (Niger).

INTRODUCTION

Cyanide is a potentially lethal poison, that is used extensively in gold mining (Cilliers and Retief, 2000; Mudder et al., 2001; Dzombak et al., 2006; US ATSDR, 2006). Accidents related to cyanide use caused disastrous environmental and health consequences through the contamination of waters, soils and foods (UNEP/OCHA, 2000). Because of its high affinity, cyanide is found in different forms in environmental matrices (US EPA, 2010; Sut et al., 2014). The determination of cyanide in these matrices before any

detection requires an extraction step (Dzombak et al., 2006). In addition, detection methods (spectrophotometric, fluorometric, titrimetric, electrochemical, etc.) suffer to multiple matrix-related interferences that can create or destroy cyanides, which is therefore very detrimental in the evaluation of total cyanide (Meeussen et al., 1989; Ma and Dasgupta, 2010; Elif et al., 2014).

To overcome this difficulty, several isolation and purification processes (photodissociation, ligand

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Figure 1. KTC, Behr Labor-Technikassure distillation apparatus. 1. Heating device, 2. Round bottom flask, 3. Filling funnel, 4. Water outlet and Water inlet, 5. Support, 6. Condenser, 7. Flow meter, 8. Absorption vessel, 9. Suction pump, 10. Bubbler, 11. Hose to the filling funnel, 12. Hose to the absorption vessel, 13. Hose to the suction pump.

exchange, ion chromatography, distillation, gas diffusion...) are used to extract total cyanide before detection (Mansfeldt and Biernath, 2000; Christison and Rohrer, 2007; Zacharis et al., 2009; Ma and Dasgupta, 2010; US EPA, 2010). The traditional way of elimination interferences and total cyanide recovery is acid distillation.

Current methods for the determination of total cyanide use different acid distillation procedures to decompose metal-cyanide complexes or any other form of cyanide (AFNOR, 1986; APHA, 1999; CEAEQ, 2016). However, many disadvantages are observed: very long procedures (1 to 2 h), tedious, energy-consuming, often with a high consumption of reagents. In addition, some procedures do not allow quantitative recovery for low concentrations.

In order to improve and to make more efficient the official procedure of acid distillation from APHA (1999) for a better cyanide extraction in the environmental matrices, a detailed investigation of optimization of the various parameters affecting the distillation was undertaken in this work. Here, the main factors governing the separation of cyanide in an aqueous medium were concerned. These are the heating temperature, the acidification pH, the extraction time, the mass or volume of the sample and the specificity of the appropriate treatment to be given to each interferent. The detection is carried out by the UV-Visible spectrophotometric method (Hassane et al., 2015) offering excellent detection.

With a view to evaluate the reproducibility of the method, recovery rates in fortified waters and soils of total cyanide were measured. The optimal conditions for complete recovery of total cyanide were taken into account in the new procedure, which was applied to

actual samples of waters from the Samira gold mine and soils.

MATERIALS AND METHODS

Analytical reagents

All the reagents used were of high analytical quality. The bi-distilled water was used for the preparation of the solutions. The solutions obtained were covered with aluminium foil to protect them from light radiation and stored in a refrigerator at 4°C.

Extraction of total cyanide

Potassium cyanide (KCN, 96%, Prolabo) and potassium ferricyanide ($K_3[Fe(CN)_6]$, 99%, RP Normapur) were served as a source of total cyanide (100 mg L^{-1}) and were dissolved in alkaline medium ($5 \cdot 10^{-2} \text{ mol L}^{-1}$) with NaOH (96%, Wagtech International LTD). Working solutions were prepared from standard solutions in the same alkaline medium. For the acidification of the extraction medium, some solutions to 50% from different concentrated acids were made in distilled water. Sulfuric acid (H_2SO_4 , 98.08%, $\rho = 1.84 \text{ g mL}^{-1}$, Fisher Scientific), nitric acid (HNO_3 , 68%, $\rho = 1.51 \text{ g mL}^{-1}$, Fisher Scientific) and hydrochloric acid (HCl, 36.4%, $\rho = 1.188 \text{ g mL}^{-1}$, Fisher Scientific) were used. To dissociate the potassium ferricyanide, a solution of magnesium chloride (2.5 mol L^{-1}) was prepared in distilled water using magnesium chloride hexahydrate ($MgCl_2 \cdot 6H_2O$, 98%, Damao Reagent) as a catalyst.

The distillation standard was prepared with 100 mL of a standard of known or unknown concentration of cyanide ion, diluted in a 250 mL volumetric flask with distilled water.

UV-Visible spectrophotometric detection

Chloramine-T trihydrate ($CH_3C_6H_4SO_2NCINa \cdot 3H_2O$, 98%, Merck) with a concentration of 10 mg L^{-1} was used for the chlorination of cyanides. A colored reagent was prepared in a 100 mL volumetric flask from 1.68 g of barbituric acid ($C_4H_4O_3N_2$, 99%, Merck) and 1.28 g of pyridine-4-carboxylic acid ($C_6H_5NO_2$, 98%, Merck) in alkaline medium (0.175 mol L^{-1}). Phenolphthalein ($C_{20}H_{14}O_4$, Merck) and ethanol (CH_3CH_2OH , $\rho = 0.791 \text{ g mL}^{-1}$, 99.7%, Merck) were used to prepare the 0.1% indicator solution. This solution was decolorized with 20% glacial acetic acid (CH_3COOH , $\rho = 1.05 \text{ g mL}^{-1}$, 99.5%, Merck).

Instrumentation

The KTC, Behr Labor-Technikassure (Figure 1) compact distillation device, was used for the extraction of total cyanide from environmental matrices. The decomposition of cyanide metal complexes by reflux heating under acidic conditions liberates hydrogen cyanide by boiling. After condensation of the vapors by cooling, the hydrogen cyanide is captured in an alkaline solution trapping of NaOH in the form of cyanide ion.

The detection of cyanide was carried out through a UV-Visible spectrophotometer (Evolution 300 UV-VIS) with quartz cuvette (Hellma 100B-QS) of $l = 1 \text{ cm}$ optical path.

Experimental procedure

A volume of 10 ml of the 0.05 M NaOH solution was introduced into the absorption vessel. 250 ml of a cyanide standard were

introduced into the distillation flask. Afterwards, the suction was adjusted so that an air bubble per second entered in the round bottom flask, corresponding to a rise of 1 cm in the absorption vessel. This airflow will transport HCN gas from the flask to the absorption vessel. Then, 25 mL of 9.2 M H₂SO₄ was introduced through the filler tube, for 3 min, the air mixes the contents of the flask. Then, 10 mL of the reagent 2.5 M MgCl₂·6H₂O was added to the reaction medium. The reaction mixture was rapidly boiled to give a reflux. This reaction mixture remained under reflux for 1 h. The number of drops falling in the round bottom flask should be between 15 and 60 drops per min. When the heating was stopped, the airflow continues for at least 15 min. The absorption solution was transferred quantitatively into a 100 mL volumetric flask and diluted to the mark with a 0.05 M NaOH solution.

This standard (20 mL) was diluted with 20 mL of 0.05 M NaOH solution in a 50 mL volumetric flask. Then, two drops of phenolphthalein (0.1%), 2 mL of glacial acetic acid (20%) followed by 1 mL of the chloramine-T trihydrate solution (10 mg L⁻¹) were added to the volumetric flask. After 2 min of reaction, 5 mL of the colored reagent was added to the medium. Finally, the volumetric flask was completed to the mark with distilled water. A colored complex of violet coloration was developed and its maximum absorbance was measured after 50 min against distilled water as a reference to the wavelength of 598 nm (Hassane et al., 2015).

Curves representations were carried out with the software Microcal Origin 6.2.

Study matrices

Non-conservative parameters such as temperature (T), electrical conductivity (EC), hydrogen potential (pH) and dissolved oxygen (DO) were measured directly *in situ*. The compositions of major ions of the different sampled waters were then determined in the laboratory.

Four types of natural waters samples (tap, river, well and pond) fortified with K₃[Fe(CN)₆] at different concentrations ranging from 0 to 5000 µg L⁻¹ were processed to assess accuracy of the proposed method of total cyanide extraction from the actual environmental matrices.

The materials used to optimize total cyanide extraction in soils were a reference soil from Fisher Scientific Company and a clayey material (LP 11) collected in the Niger River Valley. These samples, exempt to cyanide, were fortified with different contents (0 to 1000 µg g⁻¹ CN⁻) of total cyanide according to US EPA Method 9013a (2014) for the purpose of the optimization study. The pH of both soils are weakly acidic (pH ≈ 7). The standard soil contains 100% of sand and the clay material contains in addition of sand (71.6%), silt (20.8%) and clay (7.6%), therefore organic matter (Maman et al., 2017).

Total cyanide was distilled from several water samples and effluents from the Samira gold mine and the environs. The analysis concerned drinking water supplies (D1, D2, D3, D4, D5), surface water (S1, S2, S3), groundwater (G1, G2, G3) and effluents (E1, E2, E3, E4). The Samira mine is a gold mining located in southwestern Niger near the Burkina Faso border. After 15 years of open mining, it is important to evaluate the cyanide quality of the water resources of the mine and its surroundings.

Conditioning and preservation of samples

In terms of sampling, two types of conservation strategies were used, the preservation of the samples, in alkaline medium by adding two or three NaOH pellets for cyanide ion and in a neutral medium (no addition) for the major ions (MDDEPQ, 2009). These samples were stored in 500 mL polypropylene bottle. After preservation, they were kept in the refrigerator at a temperature of

4°C for not more than one week before any analysis.

Preliminary determination of major ions

The presence of ions such as: CO₃²⁻, HCO₃⁻, Ca²⁺, Mg²⁺, Cl⁻, NO₃⁻, NO₂⁻, Fe²⁺, and SO₄²⁻ influences the cyanide ion determination (Meeussen et al., 1989; Ma and Dasgupta, 2010; Elif et al., 2014). For actual samples, the preliminary determination of these interferent ions was necessary. This was important as it will better manage any interference. The determination of these ions was carried out by the methods described by APHA (1999) and Rodier et al. (2009).

Extraction of total cyanide in soils

The approach taken to optimize the distillation of total cyanide in soils was similar to that of total cyanide extraction in waters. The optimal soil mass to be introduced was that optimized in the method developed by CEAEQ (2016), which is 0.5 g.

RESULTS AND DISCUSSION

Optimization of total cyanide extraction in waters

The optimization of each parameter was carried out separately.

Optimization of the heating temperature of distillation

The optimization of the heating temperature was studied using a theoretical cyanide ion concentration [CN⁻] = 100 µg L⁻¹. At reflux, when the first drops begin to fall, the temperature was set successively at 88, 129, 161 and 181.75°C. For each heating temperature, reflux was maintained for 60 min.

The percentage of recovery (PR) of total cyanide is the ratio of the experimental concentration of the analyte to the concentration in the fortified solution. It is calculated according to the following formula:

$$\text{PR (\%)} = \frac{[\text{CN}^-]_{\text{experimental}}}{[\text{CN}^-]_{\text{introduced}}} \times 100$$

The results obtained in Figure 2 provided much information on the release of HCN during distillation at different heating temperatures. Thus, an increase in the cyanide recovery rate of the solution was observed in the temperature range of 32 to 181.75°C. At room temperature (32°C), very low cyanide release was observed. In the cyanide metal complex used (K₃[Fe(CN)₆]), a highly stable complex, the cyanide ligand is strongly bound to the iron central metal (Sut et al., 2014). This would explain the very weak dissociation of the complex. In proportion as the heating temperature increases, it is observed that the complex released more hydrogen cyanide (HCN). The release of cyanide is

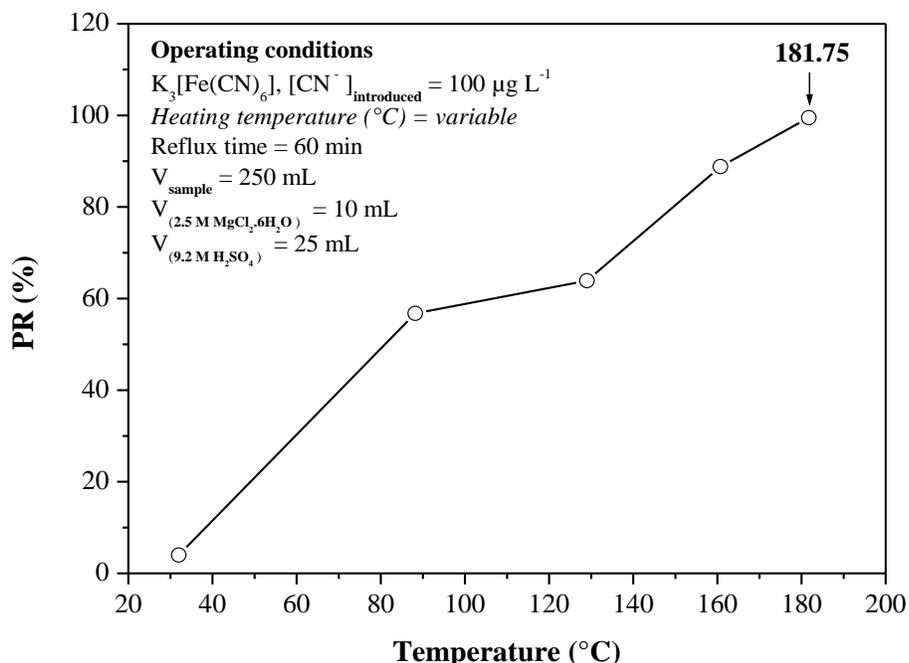


Figure 2. Percentage of recovery at different temperatures.

almost optimal around $181.75^{\circ}C$, from which temperature reached a complete dissociation resulting in a complete recovery ($\approx 100\%$).

In several and widely recognized methods (Meeussen, 1992; US EPA, 2004), the heating temperature used is often between 125 and $155^{\circ}C$. The present optimization study showed that the temperature range encountered in the literature only corresponded to a total cyanide recovery rate of between 64 and 89% . Better still, certain methods (AFNOR, 1986; APHA, 1999; CEAEQ, 2016) did not specify the heating temperature to be applied to reach reflux, inducing an additional insufficiency in the complete recovery of the total cyanide of the solution to be analyzed.

The temperature of $181.75^{\circ}C$ appeared high compared to those usually used. However, its advantage lies in the fact that it significantly improved the recovery of cyanide in the form of HCN. Thus, a heating temperature of $181.75^{\circ}C$ is required for complete recovery of total cyanide prior to the UV-Visible spectrophotometric determination of cyanide ion.

Optimization of the reflux time (extraction time)

The reflux time or time required for extraction is an important factor in the recovery of total cyanide. In the reference method and in all the other modified methods, 60 min are used for the reflux step (AFNOR, 1986; APHA, 1999; CEAEQ, 2016). In this study, in order to optimize the reflux time, different durations ranging from

15 to 75 min were investigated.

The results in Figure 3 show an improvement in the total cyanide recovery rate for reflux times between 15 and 30 min. After this time, the recovery of cyanide was almost complete; the PR remained constant up to 75 min.

The reflux time of about 60 min used by existing methods, is a relatively long time that will result in additional energy consumption. Within the context of this optimization study, the 30 min reflux time that allows equivalent recovery, is retained. Thus, the energy consumption generated by heating ($181.75^{\circ}C$) could be offset by the reflux time limited to 30 min.

Optimum extraction volume

The mass or volume of the sample can directly influence the sensitivity of a measurement. In this study, the following volumes: 100 , 150 , 200 , 250 and 300 mL were used.

From the results obtained in Figure 4, it was found that the percentage of recovery increased as a function of the volume of the solution introduced. It reaches a 100% level when the volume introduced is around 250 mL. Thus, with 100 and 200 mL of sample without dilution, as suggested by APHA (1999) and CEAEQ (2016), the recovery percentage was not optimal; it was respectively of the order of 91 and 97% . This led to incomplete recovery, hence the need to always dilute the sample to 250 mL. This dilution makes the medium more acidic, which generated a better release of hydrogen cyanide,

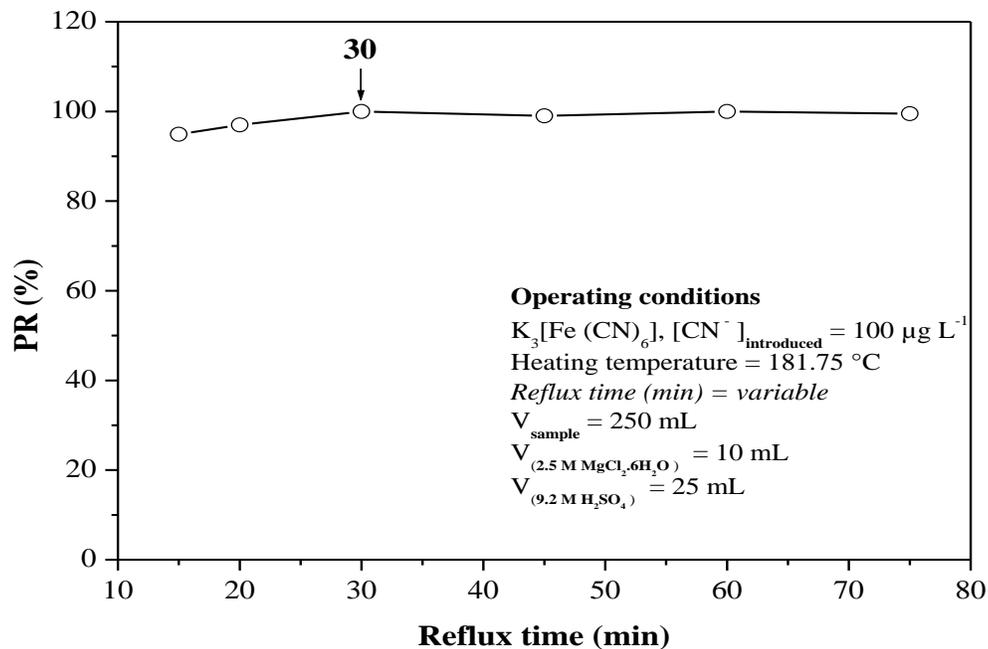


Figure 3. Percentage of recovery at different reflux times.

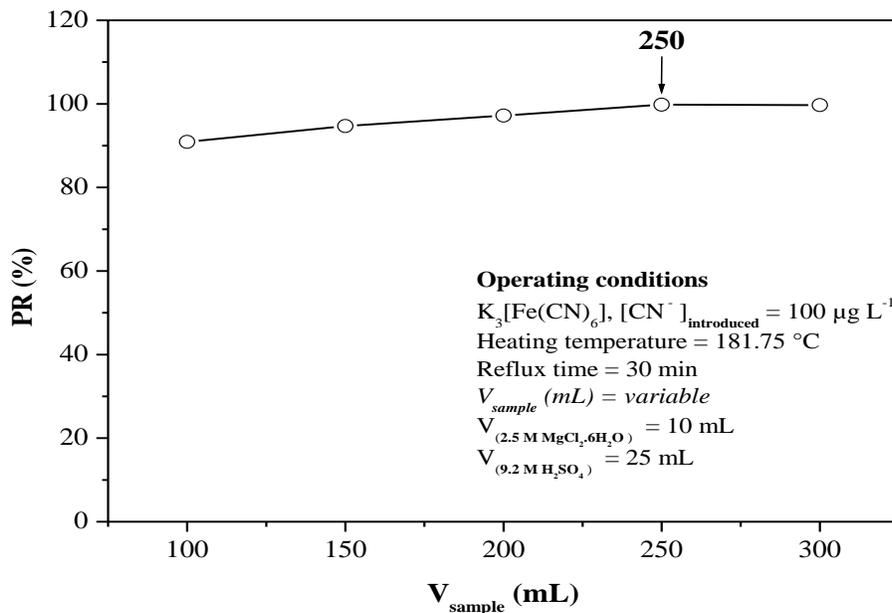


Figure 4. Percentage of recovery at different volumes.

also explaining this excellent yield.

Catalytic effect

In certain reference procedures for the extraction of

cyanide by distillation (AFNOR, 1986; APHA, 1999), magnesium chloride or mercury chloride is used as decomposition catalysts for stable cyanide metal complexes such as ferricyanide and ferrocyanide.

Once the heating temperature ($181.75^\circ C$), the reflux time (30 min) and the volume of the solution (250 ml) are

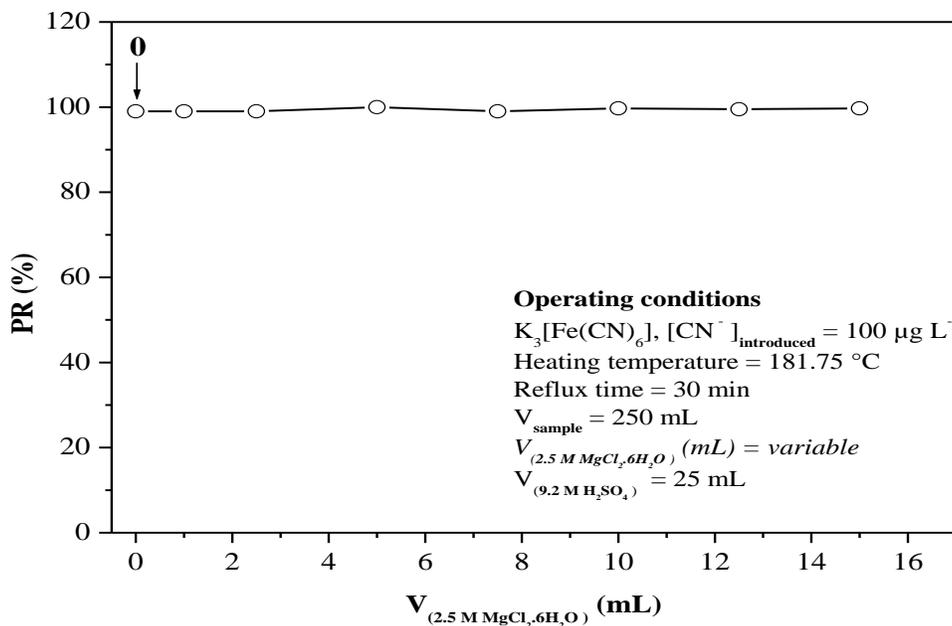


Figure 5. Percentage of recovery at different catalytic additions.

set, the catalytic effect of magnesium chloride on the recovery of cyanide ion in the extraction was studied.

Volumes from 10 to 25 mL are usually used in this step of accelerating the decomposition of cyanides. In this study, in order to optimize the contribution of the catalyst in the cyanide decomposition, different volumes of 2.5 M $MgCl_2 \cdot 6H_2O$ ranging from 0 to 15 mL were added to a standard of $K_3[Fe(CN)_6]$, $[CN^-] = 100 \mu g L^{-1}$.

The results obtained from Figure 5 showed that the presence of $HgCl_2$ - $MgCl_2$ salts in the reflux solution did not produce the expected catalytic effect in the recovery of cyanide during the extraction. The recovery percentage is of the order of 100% with or without catalyst. This result is confirmed by CEAEQ (2016).

Optimization of acidic conditions

At high pH (> 9.2), cyanide is under its non-volatile form, CN^- , at low pH it is converted to HCN, volatile (Mudder et al., 2001). The use of acid in the extraction medium promotes the release of cyanide in the form of HCN, thus allows a reinforcement of the percentage of recovery.

Traditionally, the volume of sulfuric acid used for the medium acidification step in the distillation of samples that may contain cyanide is 25 mL of 9.2 M. Here, to optimize the concentration of acid in the medium, different volumes (0 to 50 mL) of 50% acid were used for a total cyanide solution fixed at $100 \mu g L^{-1}$.

It was noted in Figure 6, a notable absence of cyanide release in the absence of acid in the medium. This demonstrates, if need be, the primordial importance of

the acidification step in the process of cyanide extraction in environmental matrices. The lower acidification of the medium (1 mL) led to a considerable recovery of cyanide ion in the form of HCN. The increasing acid addition allowed a complete recovery of cyanides during extraction. The volume of 15 mL seems to be the most adequate for improving the complete release of cyanide.

Existing methods require about 3.5 times more acid. Therefore, the use of 15 mL of H_2SO_4 (0.520 M) in the reaction medium in addition to improve the cyanide recovery rate, also allows a more rational use of the acid during extraction.

In order to optimize the nature of the acid on the recovery yield of cyanide, a comparative study was carried out between sulfuric acid and other common acids (HCl and HNO_3). The results obtained is as shown in Figure 7.

It appears that all acids allow a significant release of HCN. Therefore, HCl and HNO_3 acids can be valid substitutes for H_2SO_4 in the method.

Elimination of interferences

The elimination of interferences due to the presence of major ions is very important for a good determination of cyanide. The extraction step enables to eliminate the interferences for the determination of cyanide.

With the previous optimal conditions, the impact of interferences of the nitrate and nitrite ions of the medium was investigated.

The results in Figure 8 showed that sulfamic acid

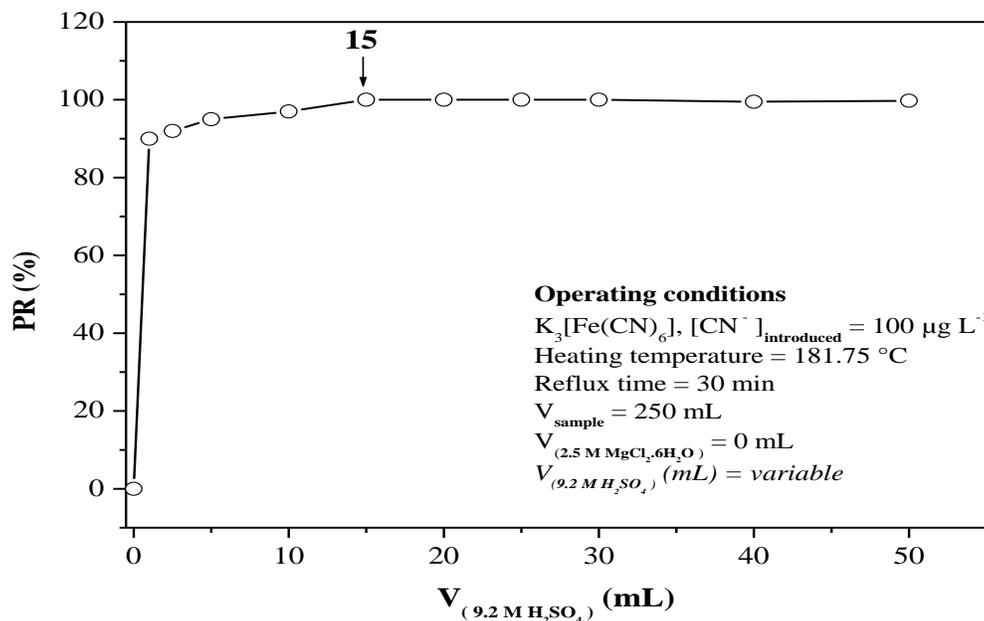


Figure 6. Percentage of recovery at different volumes of sulfuric acid.

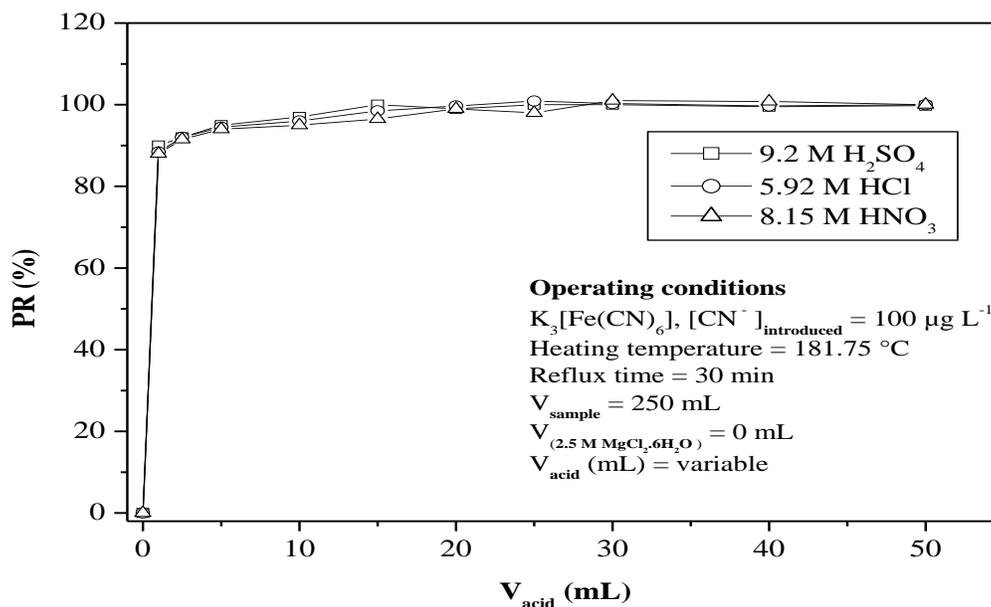


Figure 7. Percentage of recovery based on acid.

(H_3NSO_3) used in other methods to protect nitrate and nitrite interferences was unnecessary. Similarly, the use of lead carbonate ($PbCO_3$) to prevent interferences from sulphide ion was also superfluous. This helps to reduce costs but above all to avoid handling and releasing dangerous products in the environment.

Unlike the traditional methods of cyanide extraction by distillation, the present method does not use any

particular prior treatment for interferences.

Performance of the proposed procedure

The operating conditions of the new distillation method were compared with those of the traditional methods in Table 1.

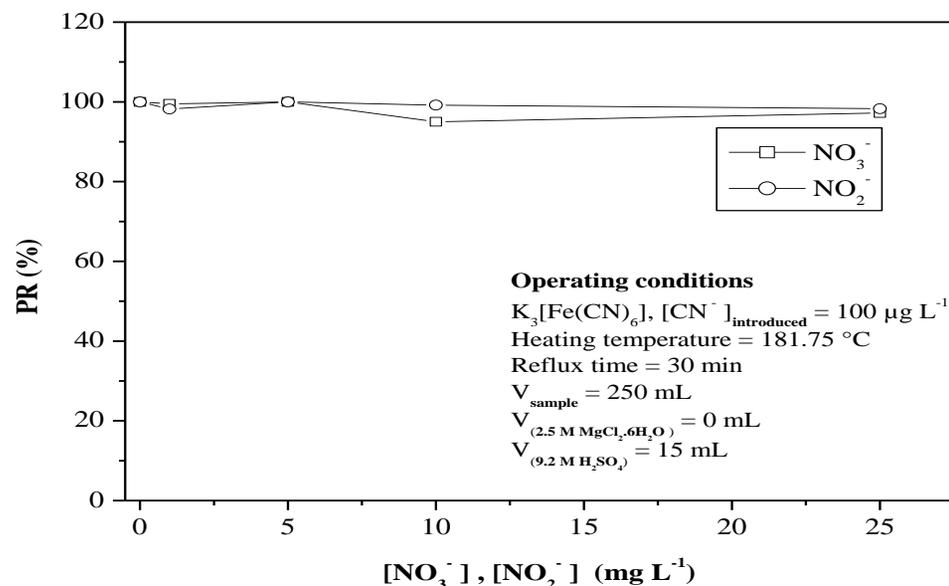


Figure 8. Percentage of recovery in the presence of interferents.

Table 1. Comparison with other methods.

Parameter	AFNOR (1986)	APHA (1999)	CEAEQ (2016)	New	Observations	
Heating temperature ($^\circ C$)	-	-	-	181.75	High temperature	
Reflux time (min)	60	60	60	30	Halving	
Analytical composition	$V_{(9.2 \text{ M } H_2SO_4)}$ (mL)	50	25	25	15	2 to 4 times less acid
	V_{sample} (mL)	100	100	200	250	Dilution
	$V_{(2.5 \text{ M } MgCl_2 \cdot 6H_2O)}$ (mL)	10	25	0	0	Without catalyst
Interference processing	Addition of reagents for particular treatments of interference			No added	No effect	

These optimal conditions obtained would completely dissociate the cyanide metal complexes

and promote complete recovery of the total cyanide.

This new proposal of distillation procedure exhibits some advantages over existing ones.

Table 2. Physico-chemical parameters of fortified natural waters.

Water sample	Tap	River	Well	Pond
pH	7.2	7.65	7.14	7.02
EC ($\mu\text{S cm}^{-1}$)	80.1	72.2	169.6	674
DO (mg L^{-1})	7.33	7.2	4.71	3.51
$[\text{CO}_3^{2-}]$ (mg L^{-1})	0	0	0	0
$[\text{HCO}_3^-]$ (mg L^{-1})	51.85	55.51	88.45	290.36
$[\text{Ca}^{2+}]$ (mg L^{-1})	8	6.5	18	55
$[\text{Mg}^{2+}]$ (mg L^{-1})	4.8	5.7	3.9	13.2
$[\text{Cl}^-]$ (mg L^{-1})	7.46	7.81	8.17	63.9
$[\text{NO}_3^-]$ (mg L^{-1})	0.34	0.53	15.3	6.3
$[\text{NO}_2^-]$ (mg L^{-1})	0.013	0.08	0.082	0.189
$[\text{Fe}^{2+}]$ (mg L^{-1})	0.062	0.287	0.807	0.55
$[\text{SO}_4^{2-}]$ (mg L^{-1})	12	24	0	192

Among other things, it saves time, energy, acid and reagents and, above all, reduces environmental impacts by avoiding the use of highly toxic substances (Pb) in the pre-treatment stage.

Optimization of extraction method in natural waters and soils

First, the physico-chemical compositions of all the natural waters used in the study were determined. The results obtained were given in Table 2. These waters had various physico-chemical properties.

These ions are at the origin of the inhibition and the exaltation of the real contents in cyanide. In particular, Fe^{2+} ion in the medium reacts with cyanide ion to form more stable cyanide-iron complexes. Thus, the determination of the cyanide of these media would require prior pretreatment or application of the operating conditions of the new distillation method.

According to the results in Tables 3 and 4, the recovery rates vary from 96 to 100%, so the decomposition of $\text{K}_3[\text{Fe}(\text{CN})_6]$ is almost complete in all fortified waters and soils as well as total cyanide recovery despite the presence of interfering ions and organic matter in these samples for low and high contents of cyanide.

The recovery rates in the Ficher soil are similar to those found in the clay material (LP 11). A large recovery as in the case of natural waters had also been obtained for soils. This confirmed the performance of the new cyanide extraction method in environmental matrices of various compositions by simple optimization of the analytical parameters.

Application on the waters of the Samira gold mine

The distillation-optimized method was applied to extract total cyanide contents in water samples (drinking, surface,

underground) and plant effluents from the Samira gold mine.

Physico-chemical composition of Samira's gold mine waters

The physico-chemical characterization of the various waters was undertaken in order to determine the interfering elements and their contents and thus, evaluate the importance of the association of the new distillation method in the determination of the total cyanide for mining samples.

The different waters had various physicochemical properties (Table 5). The pH was almost neutral for all drinking and surface waters. Pits water from open pit mining and effluents from the plant were alkaline. This alkaline nature would result from the use of very large amount of sodium hydroxide (NaOH) and lime ($\text{Ca}(\text{OH})_2$) in cyanidation. The mineralization of the waters from pits and effluents was very strong.

In addition, all waters contained relatively high levels of major ions (nitrate, nitrite, sulphate, iron, etc.) that may impact the effective cyanide ion determination in the absence of a good pretreatment of the waters samples.

Cyanide contents in Samira's waters

Waters and effluents samples from the Samira site and surroundings were placed under the same conditions as the standards and analyzed according to the new proposed procedure. They had previously undergone pretreatment by distillation under the optimal operating conditions obtained in the context of this work. Here, to further prove the effectiveness of pretreatment (distillation) which eliminates interferences by purification, in addition to total cyanide, free cyanide was determined. The concentrations of free cyanide and total cyanide in

Table 3. Percentage of recovery in natural fortified waters (Mean \pm Standard Deviation, n = 3).

Fortified water	$[\text{CN}^-]_{int}$ ($\mu\text{g L}^{-1}$)	0	50	100	200	500	1000	2000	5000
Tap	$[\text{CN}^-]_{exp}$ ($\mu\text{g L}^{-1}$)	0	49 \pm 0.5	101 \pm 1	198 \pm 5	505.17 \pm 10	1020 \pm 25	2035 \pm 15	5100 \pm 35
	PR (%)	-	98 \pm 0.01	101 \pm 1	99 \pm 2.5	101 \pm 2	102 \pm 2.5	101.75 \pm 0.75	102 \pm 0.7
River	$[\text{CN}^-]_{exp}$ ($\mu\text{g L}^{-1}$)	0.88	51 \pm 1.5	101.5 \pm 1.25	200 \pm 2	485 \pm 6	984.65 \pm 3	1947 \pm 13	4900 \pm 8
	PR (%)	-	100.25 \pm 1.25	100.65 \pm 3.75	99.57 \pm 0.56	96.85 \pm 1	98.5 \pm 0.2	97.5 \pm 0.6	98 \pm 0.2
Well	$[\text{CN}^-]_{exp}$ ($\mu\text{g L}^{-1}$)	2.13	52 \pm 3	101 \pm 3.5	203 \pm 4	480 \pm 7	971.25 \pm 10	2009 \pm 7.5	4875.5 \pm 12
	PR (%)	-	99.75 \pm 1.75	99 \pm 1.4	100.5 \pm 0.95	96 \pm 1	97.5 \pm 0.8	100.5 \pm 0.3	97.5 \pm 0.2
Pond	$[\text{CN}^-]_{exp}$ ($\mu\text{g L}^{-1}$)	3.38	52.5 \pm 4	103 \pm 5.75	205 \pm 6	501 \pm 5	982.5 \pm 8	1934 \pm 15	4850 \pm 12
	PR (%)	-	98.25 \pm 1.25	99.75 \pm 2.4	101 \pm 1.31	100.5 \pm 0.5	98.5 \pm 0.5	96.7 \pm 0.6	97 \pm 0.2

Table 4. Percentage of recovery at different cyanide contents in fortified soils (Mean \pm Standard Deviation, n = 3).

Fortified soil	$[\text{CN}^-]_{int}$ ($\mu\text{g g}^{-1}$)	0	2	5	10	20	30	50	100	200	400	1000
Soil Fischer	$[\text{CN}^-]_{exp}$ $\mu\text{g g}^{-1}$	0	1.9 \pm 0.03	4.9 \pm 0.05	9.8 \pm 0.2	20.2 \pm 0.5	29.8 \pm 0.75	50 \pm 1.5	99.8 \pm 0.8	199.2 \pm 2	398.6 \pm 1.75	994.2 \pm 4
	PR (%)	0	95 \pm 1.5	98 \pm 1	98 \pm 2	101 \pm 2.5	99.33 \pm 2.5	100 \pm 3	99.8 \pm 0.88	99.6 \pm 1	99.65 \pm 0.5	99.42 \pm 0.4
Clay LP 11	$[\text{CN}^-]_{exp}$ $\mu\text{g g}^{-1}$	0	1.8 \pm 0.04	5.1 \pm 0.04	9.9 \pm 0.25	19.8 \pm 1	30.2 \pm 0.8	49.6 \pm 1	99 \pm 1.5	199.2 \pm 2.5	396 \pm 2	996 \pm 7
	PR (%)	0	90 \pm 2	102 \pm 0.8	99 \pm 2.5	99 \pm 5	100.6 \pm 2.7	99.2 \pm 2	99 \pm 1.5	99.6 \pm 1.25	99 \pm 0.5	99.6 \pm 0.7

Table 5. Physico-chemical composition of the Samira's waters.

Water sample	pH	T ($^{\circ}\text{C}$)	EC ($\mu\text{S cm}^{-1}$)	DO (mg L^{-1})	$[\text{CO}_3^{2-}]$ (mg L^{-1})	$[\text{HCO}_3^-]$ (mg L^{-1})	$[\text{Ca}^{2+}]$ (mg L^{-1})	$[\text{Mg}^{2+}]$ (mg L^{-1})	$[\text{Cl}^-]$ (mg L^{-1})	$[\text{NO}_3^-]$ (mg L^{-1})	$[\text{NO}_2^-]$ (mg L^{-1})	$[\text{Fe}^{2+}]$ (mg L^{-1})	$[\text{SO}_4^{2-}]$ (mg L^{-1})	
Drinking	D1	7.34	36.2	72.4	6.79	0	48.8	12	4.8	8.52	9.49	1.20	0.62	38.4
	D2	7.42	38.7	71.6	6.25	0	61	15	0.6	9.94	9.95	1.04	0.75	0
	D3	7.38	37.6	801	5.13	0	341.6	76	2.04	17.75	0.863	0.034	0.18	134.4
	D4	7.73	35.2	577	5.96	0	292.8	48	24.6	15.62	1.00	0.043	0.054	72
	D5	7.5	31.6	213	7.96	0	73.2	18	6	14.2	10.33	0.018	0.109	86.4
Surface	S1	6.74	30.5	73	6.5	0	73.2	18	1.2	17.04	3.57	1.29	0.869	0
	S2	7.62	28.7	70.6	7.45	0	79.3	14	1.2	9.23	25.13	0.100	0.770	0
	S3	6.33	30	142.9	4	0	97.6	20	4.2	12.78	2.741	0.034	0.156	0

Table 5. Contd.

Underground	G1	8.82	35.2	1641	10.47	60	73.2	96	96	19.88	1.18	0.042	0.088	0
	G2	8.38	32.7	360	8.02	24	146.4	30	21	11.36	0.70	0.030	0.255	0
	G3	8.02	33.2	779	7.88	0	183	53	46.2	14.2	5.36	0.595	0.067	91.2
Effluents	E1	9.64	36.8	1687	6.6	276	378.2	40	3.6	310.98	5.87	8.474	0.077	192
	E2	9.01	36.8	1496	5.56	72	366	200	120	93.72	27.48	2.53	0.644	201.6
	E3	9.02	36.3	1490	6.37	84	341.6	280	36	93.72	27.29	5.52	0.434	182.4
	E4	9.42	36.2	1409	6.15	108	329.4	180	60	93.72	24.69	8.69	0.434	216

Table 6. Cyanide contents in waters (Mean \pm Standard Deviation, n = 3).

Water sample		[CN ⁻] ($\mu\text{g L}^{-1}$) free (without distillation)	[CN ⁻] ($\mu\text{g L}^{-1}$) total (with distillation)
Drinking	D1	0.88 \pm 0.05	4.21 \pm 0.20
	D2	2.05 \pm 0.15	3.38 \pm 0.5
	D3	0.88 \pm 0.05	0.96 \pm 0.15
	D4	0.96 \pm 0.07	3.45 \pm 0.38
	D5	0.00	0.00
Surface	S1	0.88 \pm 0.00	4.96 \pm 0.80
	S2	2.13 \pm 0.25	3.83 \pm 0.81
	S3	0.88 \pm 0.00	0.96 \pm 0.15
Underground	G1	0.88 \pm 0.00	4.8 \pm 0.63
	G2	0.88 \pm 0.00	1.96 \pm 0.15
	G3	0.88 \pm 0.00	2.04 \pm 0.10
Effluents	E1	27661.00 \pm 53.5	37057.00 \pm 51.73
	E2	182.28 \pm 0.63	945.67 \pm 2.75
	E3	486.84 \pm 6.17	1398.00 \pm 25.4
	E4	9520.00 \pm 20.00	10762.67 \pm 83.76

the different waters are shown in Table 6.

For all the samples, the relatively low concentrations of free cyanide, measured without prior distillation, compared to the high concentrations of total cyanide obtained after the

distillation process, demonstrated, on the one hand, the inhibitory effect of the presence of interfering ions on the determination of cyanide, and secondly, the effectiveness of the new technique for extracting cyanide ion from

environmental matrices. Indeed, in the absence of distillation, metallic ions such as those of iron trapped cyanide ions, explaining the relatively low levels obtained during the free cyanide assay of the samples studied.

The effluents contained in the retention structures concealed total cyanide contents up to 37 times higher than the standard discharge of only $1000 \mu\text{g L}^{-1}$ (IFC, 2007). This is a real danger. In the event of rupture or cracking of these structures, these cyanide-rich waters stored can spread over long distances and/or infiltrate the soil and contaminate water and other environmental matrices.

Thus, the different water resources, used by the near populations of the Samira mine have total cyanide contents ranging from 1 to $5 \mu\text{g L}^{-1}$. Although these concentrations were below the WHO (2008) standard of $70 \mu\text{g L}^{-1}$, they still show some contamination, for a region that would be exempt to cyanide before the mining activities.

Conclusion

This new distillation technique through its main physical and analytical parameters has made it possible to realize a great deal of deficiencies in the methods hitherto used for the extraction of total cyanide in environmental matrices.

The operating conditions are: heating temperature (181.75°C), reflux time (30 min), V_{sample} (250 mL), $V_{(2.5 \text{ M MgCl}_2 \cdot 6\text{H}_2\text{O})}$ (0 mL), $V_{(9.2 \text{ M H}_2\text{SO}_4)}$ (15 mL) and any addition of reagents for particular treatments of interference. This optimization offers a significant improvement in cyanide extraction by distillation, which reduces the numerous sources of interferences and achieves a cyanide recovery rate of around 100%. This method could be a simple, cost-effective and less expensive alternative to saving time, energy and the use of chemical reagents, compared to traditional methods that require a long procedure and very expensive.

The application of this method to the samples of the Samira gold mine proves to be satisfactory as cyanide contents in drinking water are below the WHO standard. This total cyanide extraction procedure can be applied to other matrices such as foods, physiological fluids, etc.

CONFLICT OF INTERESTS

The authors have not declared any conflict of interests.

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