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Improved determination of salicylaldoxime in water samples by liquid-liquid extraction followed by high performance liquid chromatographic analysis

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Abstract: For the determination of salicylaldoxime in environmental water samples, a stable and rapid method with low detection was proposed and established, based on the liquid-liquid extraction-high performance liquid chromatography with ultraviolet detector. Parameters including extraction solvent, ionic strength, solution pH, and extraction pattern were discussed for the optimal quantification of salicylaldoxime-spiked water. When the described method was applied to four spiked water samples, the obtained average extraction recovery rate was found between 87%–107% and relative standard deviation was below 6%. At the same time, good linear relationships were observed for spiked water samples from 0.01 to 10 μg/mL (R^2=0.9993). In addition, the detection limit of salicylaldoxime was revealed between 0.003–0.008 μg/mL, which is two orders of magnitude lower than previously reported results. Thus, the presented method may be advantageous for the high-efficiency determination of salicylaldoxime in water samples.

Key words: high-performance liquid chromatography; liquid-liquid extraction; salicylaldoxime

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1 Introduction

China is one of the largest producers and consumers of copper in the world. It produces over 2.3 million tons of copper per annum, around one fifth of the total world production [1]. In its many smelting plants, solvent extraction is the primary method in copper hydrometallurgy. Smelting and related industries, however, have particularly adverse impacts on both the environment and public health [2–4], and become some of the largest sources of environmental pollution from heavy metals even today [5], resulting in increased pollution controls for the smelter production. In recent years, organic pollutants from metallurgy process have also aroused the public concerns regarding the possible persistent effects of some organic reagents [6, 7] and some researches and practices have focused on the degradation of metal extracting reagents [8–10]. Salicylaldoxime is one of the most widely used extracting reagents in beneficiation and metallurgy fields [11–19], and its history in copper extraction can be dated back to the 1970s [11]. It also has important applications in the biological and pharmaceutical fields [20–22], fulfilling its role by blocking K^+ and Ca^{2+} currents in cardiac myocyte [23] and inhibiting the enzyme

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activity [20]. Therefore, it is critical to develop a rapid and high-efficiency method for the determination of salicylaldoxime in environmental water samples so as to serve for the understanding of its origin, migration, behavior and corresponding environmental protection.

Works relating to salicylaldoxime determination have already been described in the literature, even if such reports are still scarce. MENOYO et al [24] presented a gas chromatography-mass spectrometer (GC-MS) method for the identification of alkyl salicylaldoxime based reagents and investigated their degradation behavior by mass spectrometric analysis, which is in line with our research question. By following such an interesting work, we have performed a series of GC-MS experiments to further explore the chromatographic behavior of salicylaldoxime. However, the co-existence of four peaks in obtained chromatogram, which could be possibly attributable to the Beckmann rearrangement [25] and the dehydration reaction [26] of oxime, hindered the practical application of GC-MS method in the determination of salicylaldoxime, albeit the injector temperature was repeatedly optimized. In an alternative way, HIMBERG et al [27] developed a high performance liquid chromatography (HPLC) procedure for the determination of salicylaldoxime and β-resorcylaldoxime in human urine, using tetrahydrofuran (THF) and water (55/45, v/v) as the mobile phase and diethyl ether as the extraction solvent, respectively. This method gave a moderate extraction recovery (85%) and relatively high level limit of detection (LOD, 0.2 μg/mL). Besides, the usage of diethyl ether in this procedure readily led to a great loss and high relative standard deviation (RSD), due to its high volatility and low viscosity. Therefore, it was quite desirable and necessary to develop a reliable method with high extraction recovery and low LOD, by incorporating pre-condensation procedure and choosing right solvent.

Herein, we described a high-efficiency method for the determination of salicylaldoxime in water samples by liquid-liquid extraction (LLE) [28] prior to high performance liquid chromatography. Parameters and conditions including type and volume of extraction solvent, salt addition, pH, extraction pattern, and the components of the mobile phase were examined and optimized.

2 Materials and methods

2.1 Reagents and standards

Salicylaldoxime (98%), HPLC grade methanol, cyclohexane, toluene, ethyl acetate, diethyl ether, and dichloromethane were purchased from Aladdin (Shanghai, China). Sodium chloride (NaCl) was purchased from Sinopharm Chemical Reagent Co. Ltd (China).

Stock solutions of salicylaldoxime (1000 μg/mL) were prepared by dissolution of 50 mg salicylaldoxime solid particulates in 50 mL methanol and stored at 4 °C in the dark. Working standard solutions were prepared by serial dilutions of the stock solution with methanol prior to analysis.

2.2 Equipment and conditions for HPLC

2.2.1 Equipment

Absorbance measurements were carried out by using a TU-1901 double-beam spectrophotometer and a 1 mL quartz cell.

The HPLC-UV system was an Agilent 1260 series (Agilent Technologies, USA), equipped with a quaternary pump, a temperature controlled auto injector, and a temperature controlled column compartment.

2.2.2 Chromatographic conditions

Methanol-water (55:45, v/v) was used at 0.8 mL/min as the mobile phase with an Agilent C18 column (150 mm×4.6 mm, 5 μm) protected by a guard column with a matching stationary phase. The column temperature was 30 °C. The detection wave-length selected on the UV detector for salicylaldoxime was 305 nm. The injection volume was 10 μL. Mobile phase was filtered through a 0.22 μm membrane nylon filter (ANPEL, China), and degassed by ultra-sonication before use. Under such chromatographic conditions, the retention time of salicylaldoxime peak in the chromatogram was 4.25 min.

2.3 Liquid–liquid extraction procedure

A 10.00 mL ultra-pure water containing 30% (w/v) NaCl was placed in a 50 mL conical flask and spiked with 0.1 μg/mL of salicylaldoxime. Five milliliters of toluene were injected rapidly into the aqueous solution as the extraction solvent. After vortex mixing for 2 min, resting for 30 s and centrifuging at 5000 r/min for 5 min, the organic phase was collected, transferred to a clean tube, and evaporated to dryness under a stream of nitrogen at room temperature. 500 μL mobile phase solution was used to dissolve the dry residues, and this was filtered through 0.22 μm membrane nylon filter (ANPEL, China) prior to injection. The filtrate was transferred into a 150 μL glass insert located in a 1.5 mL liquid chromatography vial.

2.4 Statistics

The data acquired were analyzed using the Origin software package (OriginPro, v8.5, OriginLab Corporation, USA).

3 Results and discussion

3.1 Molecular fluorescence

UV absorption spectroscopy was employed to preliminarily characterize salicylaldoxime. In the ultraviolet and visible (UV absorbance) spectrum of salicylaldoxime (scanning region 190–400 nm), three absorption peaks were detected. A wavelength of 305 nm was used to minimize interference.

3.2 Chromatographic conditions

Acetonitrile and methanol were preliminarily selected as the candidates for the mobile phase. When using acetonitrile as sole mobile phase, a skewed chromatographic peak was obtained (Figure 1(a)). The sole use of methanol as mobile phase caused a strong peak tailing (Figure 1(b)). To improve the peak quality, chromatographic runs were carried out with the binary mobile phase of aqueous solution of methanol or acetonitrile. As the proportion of water increased in the binary mobile phase consisting of methanol and water, the symmetry factor was observed to increase correspondingly in an appropriate range, as indicated by Figure 1(c) (30% water, *v*/*v*) to Figure 1(d) (45% water, *v*/*v*). The latter case gave a high response with sharp peak (Figure 1(d)). In contrast, the addition of water in the aqueous-acetonitrile binary mobile phase had limited effects on the enhancement of peak shape (Figure 1(e)). To make a further comparison, the binary mobile phase comprised of THF and water (Figure 1(f)) as described in Ref. [27] was investigated to render a peak type vastly similar to that by methanol-water pair (Figure 1(d)). Considering the reproductive toxicity of THF, the methanol-water binary system was selected as the binary mobile phase in succeeding experiments. No buffers were used in the mobile phase to avoid possible side effects on the chromatographic column [29].

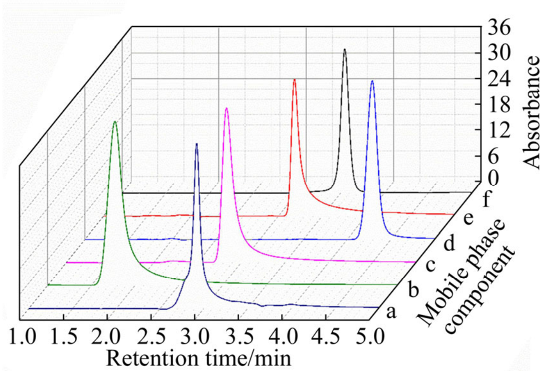


Figure 1 HPLC-UV chromatogram obtained from water sample spiked 1 μg/mL of salicylaldoxime standard solution by LLE with different mobile phase components: (a) 100% acetonitrile; (b) 100% methanol; (c) 70% methanol, 30% water; (d) 55% methanol, 45% water; (e) 55% acetonitrile, 45% water; (f) 55% THF, 45% water (*v*/*v*)

3.3 Extraction solvent and ionic strength

As known, in a LLE procedure, achieving a desirable result depends on quantity of analytes that were transferred into the organic phase [30]. According to the “like dissolves like” theory as well as the functional group structure of salicylaldoxime, four organic solvents, cyclohexane, toluene, ethyl acetate, and dichloromethane, were considered as the candidate extractants. Also, diethyl ether was included into the list in a comparative manner with previous results by HPLC method [27]. Another factor that may affect the extraction recovery and efficiency is the ionic strength in terms of salting-out effects [30, 31]. Therefore, the LLE runs were carried out under different NaCl concentrations in each candidate organic phase.

As shown in Figure 2, the initial addition of NaCl exhibited a great influence on the dichloromethane system so as to sharply raise the recovery rate to 84%. In contrast, it has much weak effects on the cyclohexane system. At lower NaCl amount (5%, *w*/*v*), dichloromethane, diethyl ether, and ethyl acetate all resulted in moderately high recovery rate (>80%). However, with further addition of NaCl, the recovery rate given by diethyl ether and ethyl acetate dropped greatly, while it kept almost steady in the case of dichloromethane. In a practical view, the high density of dichloromethane could lead to inconvenience in the removal of extraction solvent. In addition, ethyl acetate, which is slightly soluble in water, gave high standard deviation (SD) and unstable recovery rate. It was noticed that the toluene system experienced almost a positive salinity effect at higher NaCl amount (≥5%), for the recovery rate increased to 92% at 30% (*w*/*v*) NaCl amount. Thus, toluene was selected as the extraction solvent with 30% (*w*/*v*) NaCl.

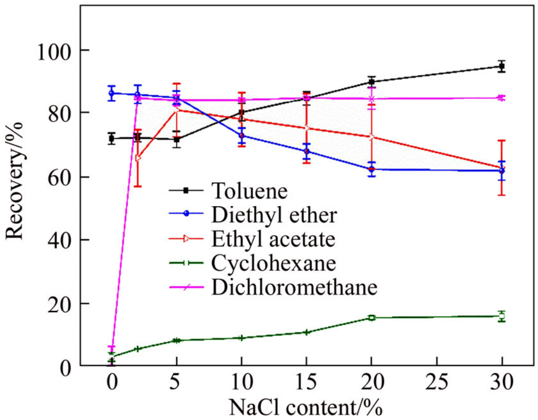


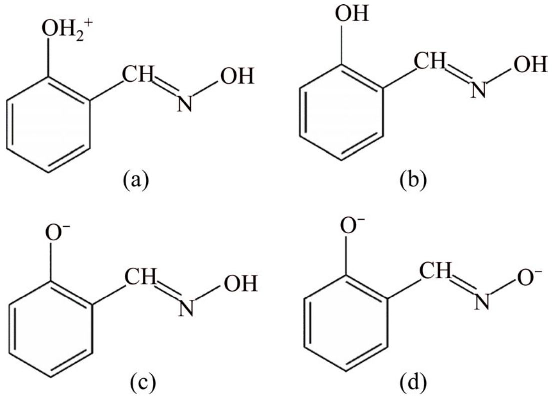
Figure 2 Effect of extraction solvent on recovery of salicylaldoxime in LLE (Extraction conditions: Water sample volume, 10 mL; extraction solvent volume: 5 mL; NaCl amount: 0%, 30% (*w*/*v*); vortex for 2 min; ambient temperature; pH 7)

3.4 Volume of extraction solvent

The volume of extraction solvent always plays an important role in LLE technology. In this study, the volume effect of extraction solvent was examined at six different levels, 0.25, 0.5, 1, 2, 5, and 10 mL, respectively. It was found that, at initial stage, the recovery rate increased drastically up to 92% with increase of toluene (<5 mL), after which the recovery curve was plateaued. Hence, the volume of toluene added to the aqueous phase was set 5 mL in subsequent experiments.

3.5 Solution pH

Salicylaldoxime contains two important functional groups: A hydroxyl group (—OH) and an oxime group (—HC=N—OH). Under different pH conditions, various molecular species of salicylaldoxime could be formed, like $C_7H_8NO_2^+$, $C_7H_7NO_2$, $C_7H_6NO_2^-$, or $C_7H_5NO_2^{2-}$ (Figure 3). TSHUMA et al [32] has investigated the equilibrium constant of salicylaldoxime in 0.5 mol/L NaCl aqueous solution at 25 °C and reported the pKa values of salicylaldoxime as 1.23, 8.55 and 11.78 [32]. To evaluate the pH influence on extraction recovery, the pH value of blank water samples was adjusted to 1, 3, 7, 9 and 12 prior to the LLE procedure. As shown in Figure 4, in the pH range 7–9, the recovery rate was nearly constant (92%). In sharp contrast, at pH 12, it decreased suddenly to 0%, which may be due to the formation of hydrophilic $C_7H_5NO_2^{2-}$ ions by releasing protons of salicylaldoxime under harsh alkaline condition. At pH 1 (near to pKa 1.23), salicylaldoxime molecules may occur either in cationic $C_7H_8NO_2^+$ or neutral $C_7H_7NO_2$ forms, so as to exhibit two peaks in chromatography. It is therefore to set pH value at 7 in next steps.



(a) (b) (c) (d)

Figure 3 Chemical structures of salicylaldoxime at different pH values: (a) $C_7H_8NO_2^+$; (b) $C_7H_7NO_2$; (c) $C_7H_6NO_2^-$; (d) $C_7H_5NO_2^{2-}$

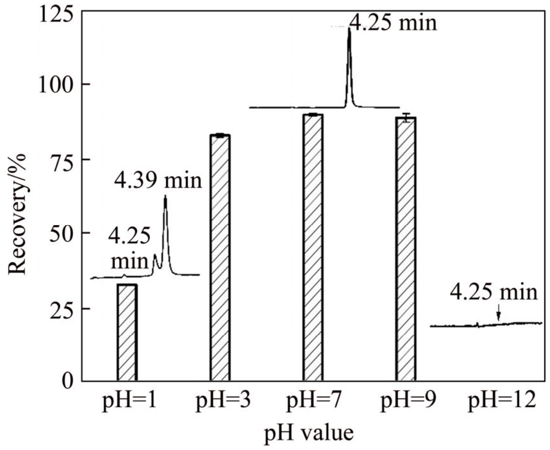


Figure 4 Effect of pH value on recovery of salicylaldoxime in LLE (Extraction conditions, as with Figure 2; toluene volume: 5 mL)

3.6 Extraction pattern

To further explore the ways to improve the extraction efficiency, LLE runs were performed under vortex [33], water bath and ultrasonic irradiation condition, respectively. As shown in Figure 5, the extraction recovery rate obtained under water bath and ultrasound assisted extraction (UAE) increased slowly with the extraction time, and reached 75% and 63%, respectively, after 60 min. In contrast, extraction aided by vortex led to a rapid and efficient process, for the recovery rate jumped to 92% only in 2 min. After that, it remained relatively stable. So, vortex was chosen as the extraction mixing method.

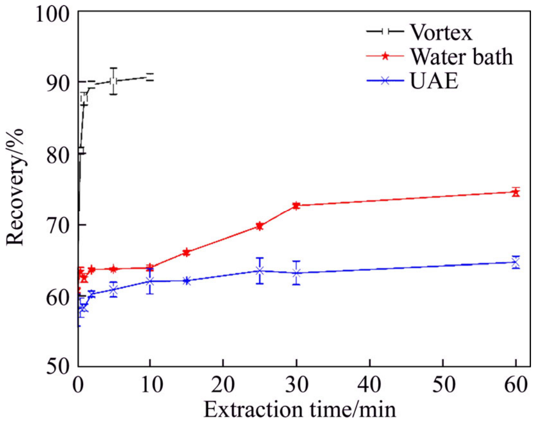


Figure 5 Effect of extraction pattern on recovery of salicylaldoxime in LLE (Extraction conditions, as with Figure 2; toluene volume: 5 mL)

3.7 Method validation

To evaluate the stability and feasibility of the developed method, an assay validation including linearity, limit of detection (LOD) and quantitation (LOQ), extraction recovery and precision was performed under optimal conditions.

The analysis of standard solution at nine concentration levels ranging from 0.2 to 100 μg/mL revealed the high linearity of the proposed method (R^2=0.9999). Similarly, for water samples spiked with salicylaldoxime, the method was also linear in 0.01–10 μg/mL range (R^2=0.9993).

The LOD, calculated at a signal-to-noise (S/N) ratio of 3 based on the peak-to-peak noise, was found between 0.003 to 0.008 μg/mL (Table 1), which is two orders of magnitude lower than those in previous HPLC work [27]. At the same time, the LOQ, based on signal-to-noise (S/N) ratio of 10 was obtained ranging from 0.012 to 0.028 μg/mL. It can be deduced then that this method is highly sensitive.

Table 1 LOD and LOQ of salicylaldoxime in four types of water sample (μg/mL)

Sample	LOD	LOQ
Ultra-pure water	0.003	0.012
Tap water	0.004	0.014
River water	0.008	0.027
Effluent	0.008	0.028

The matrix effect of the presented method was checked using real natural water samples (Table 2), including ultra-pure water, tap water, river water, as well as effluent from Xiangjiang River. Analyses of all non-spiking samples indicated the absence of salicylaldoxime. The accuracy and precision of the current method were evaluated at three spiked levels of salicylaldoxime (0.05, 0.1, and 0.25 μg/mL). As a result, reasonably high recovery rate was obtained (88.2%–105.7% for inter-batch and 87.7%–107.7% for intra-batch). In this way, the method has been validated and has been shown to be accurate and inter-batch and intra-batch precise (RSD 1.4%–4.7% and 1.4%–5.2%, respectively).

3.8 Application to real water samples

In order to demonstrate the applicability and feasibility of the proposed LLE-HPLC-UV method, samples collected from three effluent sites, respectively, as P1 (Dexing Copper Mine drain, Dexing County, Jiangxi Province, China), P2 (Wannian County Industrial Park drain, Shangrao, Jiangxi Province, China) and P3 (Ewirgol Mining Area drain, Urumchi, Xinjiang Province, China) were examined. These analyses were performed in triplicate. The identification and confirmation of peaks were performed using three criteria: 1) comparison of retention time to those of the standard solution, 2) addition of known amounts of the salicylaldoxime standard solution and observation of the increase in peak area, 3) comparison of absorption spectra with the standards using UV-vis spectrophotometer. For this analysis, P1 and P2 non-spiking samples were found to be free of salicylaldoxime contamination, while contamination were be found in P3 site at concentration of 0.078±0.001 μg/mL. Then the matrix effect was evaluated using samples spiked with salicylaldoxime standard solution (0.1 μg/mL).

Table 2 Recovery and precision of salicylaldoxime in four types of water sample (data are based on assay of 5 replicates on 3 different days)

Spiked sample	Added concentration (μg·mL^{-1})	Inter-batch (n=5)		Intra-batch (n=5)	
		(Recovery ± SD)/%	RSD/%	(Recovery ± SD)/%	RSD/%
Ultra-pure water	0.05	88.2±2.3	2.6	87.7±3.3	4.0
Ultra-pure water	0.1	95.5±1.4	1.5	95.0±3.3	3.4
Ultra-pure water	0.25	92.9±2.1	2.3	92.6±2.5	2.7
Tap water	0.05	91.2±2.0	2.2	92.2±3.2	3.5
Tap water	0.1	95.2±4.1	3.5	95.9±4.4	4.6
Tap water	0.25	89.7±3.7	4.1	90.4±3.8	4.2
River water	0.05	101.3±2.5	2.4	102.9±2.2	2.2
River water	0.1	105.7±4.9	4.7	107.7±5.6	5.2
River water	0.25	97.8±1.9	1.9	97.3±3.5	3.6
Effluent	0.05	99.2±1. 5	2.5	100.2±2.3	2.3
Effluent	0.1	100.2±1.4	1.4	102.0±2.1	2.0
Effluent	0.25	95.6±1.8	1.9	94.4±1.3	1.4

The resultant data showed that the average recoveries were between 90.4% and 92.0% with RSDs from 2.0% to 2.2% (not shown). It can be inferred from the observation of stable recovery and low RSD that the proposed method is applicable in real water samples.

4 Conclusions

In this study, a rapid, sensitive and efficient method for the determination of salicylaldoxime in the water medium was developed based on LLE-HPLC-UV technology. Parameters affecting the liquid-liquid extraction were analyzed and optimized using univariate approaches. And the optimal extraction condition is given as follows, using methanol-water system as the binary mobile phase (45% water), toluene as extraction solvent (5 mL for each run) conditioned with 30% NaCl (*w*/*v*), and performed under vortex at pH 7. The optimized LLE process, followed by HPLC-UV procedure, was applied and shown to be superior over the existed HPLC method for the determination of salicylaldoxime in water samples. The developed method is expected to be applicable to the rapid and accurate determination of title compound in environmental water.

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中文导读

水样中水杨醛肟的液-液萃取–高效液相色谱分析

摘要：水杨醛肟是一种高效、高选择性的萃取剂，广泛应用于氧化铜矿冶炼过程、生物制药工业与有机分析方面。为评估其对环境的影响，需对环境水体中水杨醛肟进行定量检测。本文基于液-液萃取–高效液相色谱（LLE-HPLC-UV）进行水样中水杨醛肟的定量分析，分别对萃取剂种类和体积、离子强度、pH 值及萃取混合方式（涡旋、水浴与超声辅助萃取）进行了优化。最终在 5 mL 甲苯作为萃取剂，NaCl 含量 30%（*w*/*v*），pH 稳定在 7 的条件下涡旋萃取 2 min，得到较高萃取率。水杨醛肟加标水样在 0.01~10 μg/mL 浓度范围内，呈现良好线性（R^2=0.9993）。该方法检出限为 0.003~0.008 μg /mL，比已有文献报导的降低两个数量级。对 4 种不同基质的水体进行加标回收实验，回收率为 87%~107%，相对标准偏差均低于 6%。说明该方法可实现水环境中对于水杨醛肟快速、稳定且高效的检测。

关键词：高效液相色谱；液-液萃取；水杨醛肟