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Rapid determination of phenolic compounds in water samples by alternating-current oscillopolarographic titration

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Abstract

A rapid, simple and sensitive method was demonstrated for the determination of phenolic compounds in water samples by alternating-current oscillopolarographic titration. With the presence of sulfuric acid, phenol could be transferred into a nitroso-compound by reacting with $NaNO_2$. The titration end-point was obtained by the formation of a sharp cut in the oscillopolarographic with infinitesimal $NaNO_2$ on double platinum electrodes. The results showed that phenol concentration had an excellent linear relationship over the range of 4.82×10^{-6}–9.65×10^{-3} mol/L, the RSD of the proposed method was lower than 1.5%, and the spiked recoveries of three real water samples were in the range of 95.6%–106.9%.

Key words: alternating-current oscillopolarographic titration; phenolic compounds

Introduction

Phenolic compounds gain great popularity due to their widespread application to produce pharmaceutical and fragrance, polymeric materials, dyes, paper, pesticides and petrochemical products etc. Therefore, it is not difficult to understand their presence in the manufacturing waters and in industrial waste from relative industries and in some of the natural waters. Due to its toxicity, they could have significant detrimental effects on water quality or animals as well as some plants even at very low level. For these reasons, some of them have been included in the lists of priority pollutants. A number of analytical techniques have been established for phenols analysis in recent years. Gas chromatography, a very sensitive and reliable analytical tool, especially in combination with mass selective detector, has been applied in separation and identification of the phenolic compounds (Angerosa *et al*., 1995). But a problem associated with this tool is that non-volatile phenolic compounds require derivatisation prior to the quantitation analysis step. High performance liquid chromatography is presently the most popular and reliable technique for the analysis of phenolic compounds. Often used detectors usually are the UV, electrochemical detector and colorimetric detector (Tasioula-Margari and okogeri, 2001; Bendini *et al*., 2003; Akasbi *et al*., 1993; Wilkinson *et al*., 2002; Bonnely *et al*., 2000). More recently, LC-MS has been developed to be a robust and valuable instrumental analytical method for the determination of many compounds including phenolic compounds, which possesses the merit that does not require the analytes must be volatile and has been considered as an ideal tool in analytical, medical, and environmental and other fields. However, it is very expensive and needs high requirement for the operator. Up to now, it cannot be employed as common instrument for routine analysis (Watanabe and Terable, 2000). Capillary electrophoresis (CE), another alternative analytical technique, has also been utilized for the analysis of these compounds (Bonoli *et al*., 2003; Vaher and Koel, 2003; Demianova *et al*., 2003). It can provide many strongpoints such as high separation efficiency, small sample and electrolyte consumption and rapid analysis. These merits make CE of great utility in routine analysis and monitoring processes in a number of industrial fields. Moreover, CE is relatively well suited to analysis of complex samples, and it allows in-capillary concentration such as electrokinetic stacking (Kuban *et al*., 2002), sweeping, dynamic pH junction, and anion or cation selective exhaust injection-sweeping-MEKC, and dynamic pH junction-sweeping etc. Recently, CE has been shown to be a powerful and efficient technique and also applied to separate the EPA 11 priority phenols successfully (Groom and Luong, 1997; Zemann and Volgger, 1997; Martinez *et al*., 1996). In addition, instrumental methods, biological

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methods have been improved to be very useful in the analysis of phenols in food and environmental samples etc. Among these, biosensors are the popular and gain more attention in recent years. A great deal of biosensors has been developed for determination of phenols, which are on the basis of tyrosinase and perodidase (Serra *et al*., 2002; Cummings *et al*., 2001; Mai Anh *et al*., 2002; Campuzano *et al*., 2003; Zhang *et al*., 2001; Gaspar *et al*., 2001; Liu and Ju, 2002; Ferapontova and Puganova, 2002; Huang and Hu, 2001). However, these enzymes require strict conditions for keeping and using as well as transporting, all these make it inconvenient to establish and apply these bio-methods.

Alternating-current oscillopolarographic titration has been developed to be a simple, rapid, sensitive and inexpensive analytical tool in recent years (Zhan and Zhao, 1999), and it has had many applications in analytical, food and environmental fields. $NaNO_2$ has been reported as a multifunction reagent for titration, and $NaNO_2$ in minute quantities can exhibit a sharp cut in an alternating-current oscillopolarograph (Zhan, 1992). Moreover, Li (1996) has reported that phenol can be transferred into a *p*-nitroso-phenol with reaction with $NaNO_2$ under sulfuric acid and low temperature conditions. On the basis of this experimental principle, a new, simple, rapid, and sensitive determination method was conceived for phenols in water samples without using expensive instruments by exploiting the emergence of a sharp cut of $NaNO_2$ on the platinum electrodes in an alternating-current oscillopolarograph.

The aim of present work was to establish a rapid and sensitive method for the direct analysis of phenols with an alternating-current oscillopolargraph. Several parameters governing the emergence of a sharp cut were optimized. The phenols detected with proposed method should be all the phenols that can react with $NaNO_2$ and transfer into corresponding nitroso-compound at low temperature and sulfuric acid conditions. In order to simplify the experimental procedure, phenol was selected to use as the model compound for method development.

1 Experimental

1.1 Reagents and chemicals

Phenol was obtained from the Third Chemical Factory of Jiaozuo. Methanol was purchased from Scharlau Chemie SA (sulfanilic acid; high pure grade), sodium nitrite, potassium bromide, hydrochloric acid, acetic acid, sodium thiosulfate were of analytical grade. If not stated, the other reagents used were also of analytical grade.

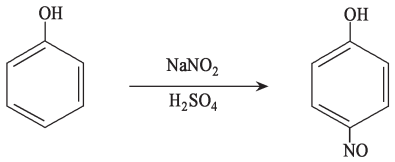
Dissolving 0.49 g of phenol in deionized water and then transferring into a 50-ml volumetric flask to obtain a stock solution of phenol with a concentration of 0.096 mol/L, and this stock solution was calibrated with sodium thiosulfonate before use. Before preparing a stock solution of sodium nitrite, sodium nitrite was dried to a constant weight at 105°C, and a certain amount of sodium nitrite was weighted and dissolved in deionized water for a concentration of 0.12 mol/L after the temperature was lowered to room temperature. These stock solutions were stored at 4°C. Standard working solutions at various concentrations were prepared daily by appropriate dilution of aliquots of the stock solution. The standard solution of sodium nitrite was calibrated with sulfanilic acid solution before use. The non-phenol water used in the experiment was prepared as follows: adding 0.2 g activated carbon into 1 L ultra-pure water, and then shaking for a certain time, and keeping 24 h, and thereafter filtrating to obtain the filtrate, which was stocked in glass bottle for further use.

1.2 Apparatus

A LS-1A alternating-current oscillopolarograph (the Seventh Shandong Telecommunication Factorary, Jining, China) was used throughout the experiment. An 81-2 magnetic stirrer (Shanghai Sile Instrument Factory, China) was used for complete reactions. The used micro platinum electrode and platinum sheet electrode in the further experiments were self-made in our laboratory.

1.3 Principle

According to the report (Li, 1996), phenol could be reacted with sodium nitrite under the presence of sulfuric acid and at low temperature (near zero centigrade), and phenol was transferred into *p*-niroso-phenol, meanwhile, acetic acid was reported that could accelerate the reaction procedure. The procedure can be simply shown as follows:



On the basis of the above reaction principle, sodium nitrite is an important reactant, when phenol is completely transferred into stable *p*-nitroso-phenol, a very small quantity of sodium nitrite in excessiveness will produce an acute cut on the micro-platinum and platinum sheet electrodes in the alternating-current oscillopolarograph, and the emergence of an acute cut can be used as an indication marker of the end-point of titration coming. Therefore, proposed method was established based on this reaction principle and the coming of the end point of titration.

1.4 Procedure

Twenty-five milliliters deionized water, 1.5 g of potassium bromide and 40 ml of 2.5 mol/L sulfuric acid were mixed in a 100-ml beaker, outside the beaker, a Petri dish filled ice and water was used for keeping the temperature desired for the reaction. The platinum electrodes were placed in the beaker and the magnetic stirrer was turned on. Titration was then carried out very slowly until the emergence of an acute cut. When a phenol solution was used instead of deionized water, the process was the same. The quantity of sodium nitrite used in each step was recorded, and the real concentration of phenol in the sample could be calculated based on these data. Fig.1 is

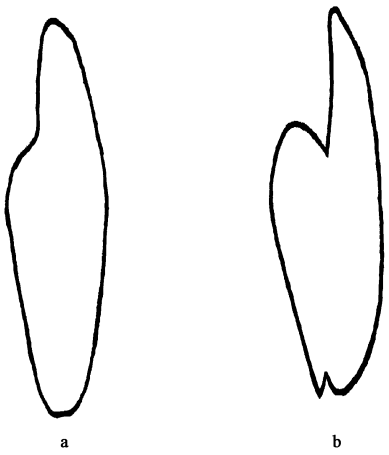


Fig. 1 Oscillopolarogram before titration (a) and at the titration endpoint (b).

the oscillopolarograms of no titration and the titration endpoint, respectively.

2 Results and discussion

2.1 Composition of substrate

2.1.1 Quantity of potassium bromide

The effect of potassium bromide was investigated with the quantity of potassium bromide changing in the range of 0.3–1.5 g under the conditions that sulfuric acid was kept at a constant content of 40 ml (2.5 mol/L H_2SO_4) and deinized water 20 ml. The results are shown in Fig.2, it indicates that with an increase of potassium bromide the needed volume of sodium nitrite decreased over the range. The best result was obtained when the amount of potassium bromide was 1.5 g. Therefore, 1.5 g of potassium bromide was used in further experiments.

2.1.2 Optimization of the pH

From the procedure section, phenol could react with $NaNO_2$ under an acidic environment and low temperature. Thus, the pH value would be a crucial factor in this reaction, and has a direct impact on the reaction rate.

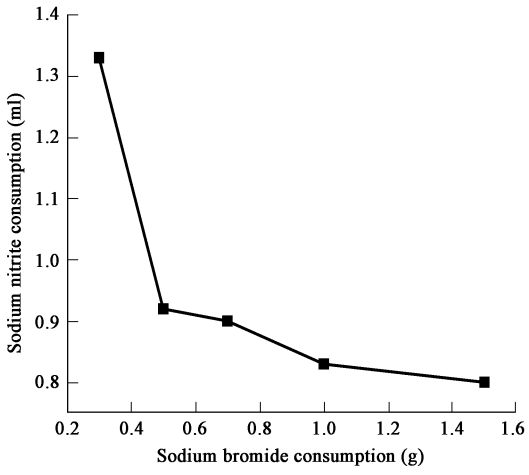


Fig. 2 Effect of the amount of KBr on the consumption of $NaNO_2$.

In order to obtain reasonable reaction conditions and a high reaction rate, different acids were investigated for the employment in the method. In the reaction mentioned above, sulfuric acid was used for gaining ideal reaction procedure. From the reaction equation, sulfuric acid was used only for providing acid media. In our experiments, sulfuric acid and hydrochloric acid all give better results and the cut of endpoint emerge very rapidly, meanwhile, the required volume of sodium nitrite is almost as the same under identical conditions. These results were well in agreement with the estimation. In theory, nitric acid should also be utilized for providing acid environment, yet nitric acid could react with phenol to produce nitroso-phenol under the catalysis of sodium nitrite (Wei *et al*., 1997), therefore nitric acid was not considered for further use. Based on the results from Li (1996), mixture of sulfuric acid and acetic acid was also examined for rapid and sensitive reaction, but the results indicated that the cut of the oscillopolarograph of $NaNO_2$ emerged very slowly with markedly delay. So sulfuric acid was employed in the following experiments. The concentration and volume of sulfuric acid were optimized in the range of 1–3 mol/L and 15–40 ml, respectively shown in Tables 1 and 2. The results showed that the reaction rate was very low, so the reaction time was prolonged, and only some of phenol was transmitted into a nitrous compound when the concentration of sulfuric acid was too low or the volume of sulfuric acid was too small. However, the excellent results could be obtained when the concentration and volume of sulfuric acid were in the range of 2–3 mol/L and 30–40 ml, respectively. So, 40 ml of 2.5 mol/L sulfuric acid was chosen in the following work.

2.2 Influence of $NaNO_2$ concentration

In general, the higher is the concentration of $NaNO_2$, the easier does it reach the end point of titration. However, too high a concentration of $NaNO_2$ resulted in a difficulty to determine the end point of titration exactly, owing to a significant difference in the concentration of the target compound, and a large error would occur. On the contrary, according to a previous report (Dong *et al*., 1997), $NaNO_2$ decreased due to volatilization when its concentration was too high, which made the error increase. Low concentration of $NaNO_2$ could not achieve better results, because it made a sharp cut, and the end point of the titration emerge very slowly and consume too much $NaNO_2$ that changed the environment significantly. To investigate the influence of the concentration of $NaNO_2$, a series of experiments were designed with a phenol concentration of 9.65×10^{-4} mol/L. The results indicated that it was suitable for phenol determination when the concentration of $NaNO_2$ changed in the range of 0.0121–0.0145 mol/L. In this study 0.0121 mol/L was employed for use.

2.3 Selection of the reaction time

Reasonable reaction time is one of the key factors that determine an accurate analysis. Long time reaction might result in a loss of $NaNO_2$ and phenol due to volatilization, which makes the consumption of $NaNO_2$ increase and

Table 1 Effect of the concentration of H_2SO_4 solution ($V_{H_2SO_4}$=40 ml)

H_2SO_4 (mol/L)	KBr (g)	Added phenol (mol/L)	Detected (mol/L)	Relative error (%)
1.0	1.5	9.647×10^{-6}	1.044×10^{-5}	+8.22
1.5	1.5	9.647×10^{-6}	1.032×10^{-5}	+6.98
2.0	1.5	9.647×10^{-6}	9.833×10^{-6}	+1.93
2.5	1.5	9.647×10^{-6}	9.591×10^{-6}	–0.58
3.0	1.5	9.647×10^{-6}	9.712×10^{-6}	+0.67

Table 2 Effect of the volume of H_2SO_4 solution ($C_{H_2SO_4}$=2.5 mol/L)

H_2SO_4 (ml)	KBr (g)	Added phenol (mol/L)	Detected (mol/L)	Relative error (%)
15	1.5	9.647×10^{-6}	1.056×10^{-5}	+9.46
20	1.5	9.647×10^{-6}	1.032×10^{-5}	+6.98
25	1.5	9.647×10^{-6}	1.008×10^{-5}	+4.45
30	1.5	9.647×10^{-6}	9.833×10^{-5}	+1.93
35	1.5	9.647×10^{-6}	9.712×10^{-6}	+0.67
40	1.5	9.647×10^{-6}	9.591×10^{-6}	–0.58

large error. However, very short reaction time may lead to an incomplete reaction. In this work, the reaction time was optimized within the range of 0–5 min with all other conditions being constant. The results indicated that excellent performance was over 1 min. So, 2 min was used as the optimal reaction time.

2.4 Effect of reaction temperature

The temperature is an important factor for a chemical reaction. The method in this study is on the basis of the reaction of sodium nitrite and phenol under acidic condition, therefore, the temperature will be of a great importance for the method development. An investigation was carried out to select the optimal temperature. The experimental results indicated that excellent results were easily obtained when the temperature was in the range of 0–5°C, and the cut of endpoint emerged very slowly and the consumption of sodium nitrite would increase when the reaction temperature was over 5°C. This was as the same as reported by Li (1996), which had exhibited that the target reaction was processed very well with the temperature range of 0–5°C. On the other hand, sodium nitrite will transfer into nitrous acid and decompose under strong acidic condition when reaction temperature was too high. Hence, the experimental temperature was controlled in the range of 0–5°C by ice and water for further study.

2.5 Interference of the concomitant ions and organic compounds

Presently, it is a very important aspect to investigate the interference of any potential concomitant ions or organic compounds to validate the proposed method. The presence of concomitant ions or organic compounds probably affect the correctness of analysis with the proposed method. Therefore, it is a crucial procedure to carry out such investigation. A series of experiments were designed with the concentration of phenol kept at 9.65×10^{-3} mol/L and the relatively error was limited to no more than ±2%. The results are listed in Table 3. As can be seen, most ions and organic compounds have no significant influence on the analytical results.

Table 3 Interference of concomitant ions or organic compounds on the determination of phenol

Fold	Concomitant ion or organic compound	Interference
0.02	NO_3^-, sulfururea	–
0.2	Hg^{2+}	–
1.5	Fe^{3+}, Ni^{2+}, Cu^{2+}	–
30	Dichloromethane	–
200	Mn^{2+}	–
250	Zn^{2+}	–
400	Al^{3+}, EDTA, $Cr_2O_7^{2+}$	–
8000	Na^+, Cl^-	–
1.2×10^{-3}	Ethanol	–
1.2×10^{-5}	Methanol	–

–: No interference.

2.6 Reproducibility, linear range and detection limit

The reproducibility of the proposed method was studied for eight replicate experiments for a sample spiked at 9.65×10^{-3} mol/L of phenol, and the linear range and detection limit were investigated using a series of standard solutions of phenol at different concentrations. The relative standard deviation (RSD) was 1.5% (n=8). A better linear relationship was found over the range of 4.82×10^{-6}–9.65×10^{-3} mol/L, and the coefficient of correlation was 99.998%. The detection limit was obtained as 9.647×10^{-7} mol/L.

2.7 Recovery and sample analysis

The proposed method was also applied to real sample analysis. Three water samples, such as tap water, reservoir water and lake water, were collected for validating. Tap water was collected from our lab, and reservoir water and lake water were obtained from a nearby reservoir and lake nearby. These samples were analyzed after simple filtering with a 0.45-μm micropore membrane, and no phenol was found. All these water samples were kept for use at 4°C. Further, spiked recovery experiments were performed for checking the utility of the proposed method with three different concentrations of phenol. The results demonstrated in Table 4. From the Table, the recoveries of the three water samples were satisfactory. Hence, this method can be used in a real environmental water analysis

Table 4 Spiked recoveries of phenol with three concentrations in three realworld samples

Water sample	Added (mol)	Detected (mol)	Recovery (%)
Tap water	1.9294×10^{-3}	2.0638×10^{-3}	106.97
		1.9492×10^{-3}	100.67
		1.8210×10^{-3}	94.38
	4.8235×10^{-3}	4.6132×10^{-3}	95.64
		4.7346×10^{-3}	98.16
		4.8560×10^{-3}	100.67
	9.6470×10^{-3}	9.8334×10^{-3}	101.93
		9.4692×10^{-3}	98.16
		9.7120×10^{-3}	100.67
Reservoir water	1.9294×10^{-3}	1.8210×10^{-3}	94.38
		2.0638×10^{-3}	106.97
		2.0638×10^{-3}	106.97
	4.8235×10^{-3}	4.6132×10^{-3}	95.64
		4.8560×10^{-3}	100.67
		4.6132×10^{-3}	95.64
	9.6470×10^{-3}	9.8334×10^{-3}	101.93
		9.8334×10^{-3}	101.93
		9.4692×10^{-3}	98.16
Lake water	1.9294×10^{-3}	2.0638×10^{-3}	106.97
		1.8210×10^{-3}	94.38
		2.0638×10^{-3}	106.97
	4.8235×10^{-3}	5.0988×10^{-3}	105.70
		4.6132×10^{-3}	95.64
		4.7346×10^{-3}	98.16
	9.6470×10^{-3}	9.9548×10^{-3}	103.19
		9.8334×10^{-3}	101.96
		9.5906×10^{-3}	99.42

for phenol determination.

3 Conclusions

Phenolic compounds are important priority pollutants in most countries in the world, and many related analytical techniques have been developed for detection of phenols. But they require expensive instruments or a procedure of derivatization or analysis process time-consuming. Present work established a novel method for phenols determination based on alternating-current oscillopolarographic titration without any derivative process. The affecting factors were investigated and optimized, and the optimal conditions were as follows: the substrate consisted of 40 ml of 2.5 mol/L sulfuric acid and 1.5 g of KBr, the concentration of $NaNO_2$ was set at 0.0121 mol/L, and 2 min was taken as the reaction time. The reaction temperature was controlled over the range of 0–5°C. The experimental results had demonstrated that this method offered excellent recoveries and could be employed for environmental sample analysis. In view of the rapidity, sensitivity, simplicity, environment-friendly nature and so on, the proposed method will be an excellent alternative detection technology for phenol analysis, and will be widely employed in environmental and other related fields.

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