NOTE

Spectrophotometric Determination of Trace Volatile Phenol in Water Samples

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Using a surface active agent Triton X-100 instead of CHCl₃ as extraction agent, utilize the cloud point phenomena, under the optimum condition, spectrophotometry was used to determine the phenol quantity in enriched phase. The maximum absorption of colour substance is at $\lambda_{max} = 480$ nm. $\varepsilon = 3.25 \times 10^5$, Beer's law is followed in the content scope of 0-2.8 mg/L of volatile phenol. Detection limit of the method was 2.0 µg/L. The determination of volatile phenol in surface and irrigate water was performed and the standard addition recovery of volatile phenol was 95.9 % -103.6 %. The relative standard deviation of 10 replicate determinations was 2.15 %-2.49 %. The accuracy and precision were all satisfactory.

Key Words: Cloud point extraction, Volatile phenol, Spectrophotometry.

Determination of trace phenol commonly used chloroform as the extractive agent, but chloroform has smell, toxicity and volatility, which has damage on the heart, liver, kidney and central nervous system. The damage can be caused by poisoning through the skin absorption or breath. Chloroform can indirectly cause cancer by damaging cells[1]. This research carried out enrichment of volatile phenol by using surfactant Triton X-100 as the extractant which is non-toxic, tasteless and non-volatile to perform cloud point extraction and by spectrophotometric determination. Up till now, more reports by this extraction method are on metallic elements determination and there is no report available on volatile phenol.

Principle: When non-ionic surfactant solution is heated to a temperature, the solution appears turbid and phase separated, this is stated as cloud point phenomenon, the temperature used is called the cloud point temperature. Dissolved in the solution the hydrophobic material combine with hydrophobic groups of surfactant, when the phase separation happend it was extracted into the surfactant phase, while the hydrophilic material remained in the aqueous phase, as the volume of surfactant phase is much smaller than the water phase, the analyse aim component was enriched and separated from the matrix, this method is called cloud point extraction. The cloud point phenomenon is due to the binding force of hydrogen bonds can not keep the water molecules attached to the oxygen atom of ether with increasing temperature[2,3].

1 g/L phenol of standard stock solution; NH₃-NH₄Cl buffer solution at pH 10; 4-amino antipyrine solution of 2 %;

potassium ferricyanide solution of 8 %; Trition X-100 solution of 12 %. In 50 mL colourimetric tubes, 3 mL of 7.40 µg/mL standard phenol solution, 0.50 mL of ammonia-ammonium chloride buffer solution at pH 10, 1 mL of 4-amino antipyrine solution of 2 % was added and then mixed. 1 mL of potassium ferricyanide solution of 8 % was added and mix well. After ten minutes stood, add 1.6 mL of Triton X-100 solution of 12 %, the resulting solution was diluted to the mark and shaken up. Heated 30 min in 95 ℃ water bath, discard the water phase, use phenol-free water to dilute organic phase to 10.00 mL, the absorbance of coloured solution was determined in 2 cm cells at 480 nm using the reagent blank as reference (721 E-type spectrophotometer).

Absorption curve and measurement wavelength choice: The absorption curve is shown as Fig. 1. For the phenol colour material *vs*. reagent blank, the maximum absorption of phenol colour material is at 480 nm. Thus, 480 nm was chosen as the measurement wavelength.

Influence of pH value of buffer system: The experiments show that when using ammonia-ammonium chloride buffer solution to controll pH, the solution is clear and the colour reveal is normal with the pH between 10-11. In the other pH, potassium ferricyanide can decompose and precipitate easily when heating applied. Therefore, 0.5 mL of ammonia-ammonium chloride buffer solution was chosen.

Influence of Triton X-100 dosage: When using 1.4-1.8 mL of 12 % Triton X-100 solution, the absorbance can keep probably same, so choose 1.6 mL as the best volume of 12 %

TABLE-2
SAMPLE RETURN-RATIO

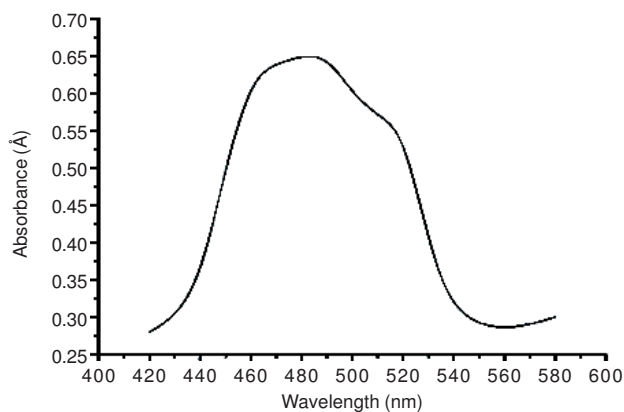| Sample	Measured values after adding 10 µg phenol (µg)	Values of wate samples (µg)	The amount of measured (µg)	Relative standard deviation (%)	Recovery (%)
Irrigate	18.45, 18.30, 18.35, 18.42, 18.42 18.41, 18.40, 18.30, 18.34, 18.33	8.78	9.59	2.49	95.9
River	18.87, 18.70, 18.78, 18.70, 18.86 18.88, 18.75, 18.77, 18.86, 18.77	8.44	10.35	2.15	103.5

Fig. 1. Absorption curve

Triton X-100 solution adding, at this point the concentration of Triton X-100 was 6.4 %.

Influence of heating temperature and time: At 90 ℃ and 95 ℃ temperature conditions, some tests were done with different heating time. It is shown that too long heating time will led precipitation take place, too short heating time will get no complete phase separation. The optimal heating time was 30- 35 min under 95 ℃.

Influence of centrifuge: A set tests under the optimum conditions, in different centrifugation speed and time, shown the influence of water separation with or without centrifuge on the absorbance. The results shown that the centrifugal is good for water separation, but it also lower the sample temperature, it is negative to phase separation. So centrifuge has little effect on the absorbance, so direct separation after water bath heating can be used.

Influence of adding additives: Some literature reported that the addition of some inorganic electrolytes into non-ionic surfactant solution can decrease the cloud point[4]. Taking time and energy saving into account, some tests by adding additives (*e.g.*, Na_2SO_4, $MgSO_4$, $NaNO_3$, $ZnSO_4$ *etc.*) were conducted. The results show that although the cloud point by adding additives can be reduced from 90 ℃ to 75 ℃, but the absorbance values decreased 50 % to 8 % or so. To ensure the determination sensitivity, no adding additives is needed.

System stability test: Stable time of coloured substances of national standard aqueous system is 10 to 30 min, chloroform system is 10 min to 3 h. Results show that the fluctuations of the absorbance values are less than 2.6 % in 10 min to 4 h in this new system.

Interference experiment: Under the optimum conditions, adding different ions into the 0.89 µg/mL of phenol, when measured relative error less than ± 5 %, the allow coexist ion multiples (in mass multiply) are shown in Table-1.

TABLE-1
DISTURBANCE MATTER PERMISSION MULTIPLE

Coexistence properties	Allow multiple	Coexistence properties	Allow multiple
K^+, Na^+, SO_4^{2-}, NO_3^-, NH_4^+, NO_2^-	1000	Methanol, ethanol	200
Zn^{2+}, Mg^{2+}, Al^{3+},	500	Benzoic acid	150
Ca^{2+}, Cu^{2+}, Ba^{2+}, Fe^{2+}	100	Benzene, toluene	40
Cd^{2+}, Pb^{2+}, Cl^-	50	Aniline, diphenylamine, SA	10
Fe^{3-}, Cr(VI), SO_3^{3-}, Cr^{3+}, S^{2-} Ni^{2+}	20	Acetaldehyde acetic acid	5

Linear regression equations and sensitivity: Results show that: the linear regression equation the of this new method was A = 0.029C (µg) + 0.011, correlation coefficient r = 0.9991, within 0-2.8 mg/L scope the Beer's law is obeyed, the molar absorption coefficient $\varepsilon = 3.25 \times 10^5$. The test was repeated 20 times, according to 3σ/K method, the detection limit is 2 µg/L. The linear regression equation of chloroform extraction system was A = 0.027C (µg) + 0.010, r = 0.9990, within 0-1.2 mg/L scope, Beer's law is obeyed. Therefore, this cloud point extraction method could replace the conventional chloroform extraction, the sensitivity and linear range were slightly better than chloroform extraction system.

Sample analysis and methods precision check: Taking pre-distilled water samples 25 mL to measure under the best conditions, the results were shown in Table-2. The measuring results show that the accuracy and precision of this method can meet the requirement of water sample checking.

Conclusion

This new system is using surfactant Triton X-100 to replace chloroform to extract trace phenol, its sensitivity, linear range and correlation are slightly better than the national standard method. This extractants are non-toxic, tasteless, non-volatile and harmless to operator and environment. One sample needs only 0.2 mL of extraction solvent (compare with chloroform, 30 mL extraction to be needed), by this way the sample checking cost can be reduced and this new method is adapted to the green analysis technique development.

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