Progress of optical determination for phenolic compounds in sewage

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Abstract—The harm of the phenolic compounds to environment was discussed in this paper. The progress of international methods for phenolic compounds was reviewed from 1938 to the end of 1995. The references dealt mainly with the progress of study on optical determining methods, e. g. visible-, UV-, derivative-, fluorescent-, infrared absorptive-, atomic absorptive photometries for phenolic compounds in waste water, and application of the above-mentioned methods in environmental monitoring.

Keywords: phenols; optical determination methods; sewage.

1 Introduction

Phenolic compounds belong to the second class of pollutants (NEPBC, 1989) in environment. Phenols are mainly from the waste water in refinery, cokery, gasworks, paper mill, pharmaceutical factory and chemical plant *etc*. (Wei, 1990), and also from the catabolism of natural or chemical products (Bai, 1984), e. g. pesticide (insecticide, germicide, herbicide *etc*.). Phenols are harmful to personal health and affect the breeding of hydrobios, due to the smell and toxicity (Willen, 1977). Therefore, phenols are monitored as important organic pollutants in the world (JSA, 1977; Mills, 1971; Deutsche, 1984; APHA, 1985) and so do by China (CEMH, 1984).

There are many kinds of phenols (e. g. mono-, binary-, polyhydric-phenols, polysubstituent and polysubstituted phenols and their isomer *etc*.) (Elsenstaedt, 1943). In this paper, only the volatile phenols whose b. p. are below 230℃ and which can be distilled out with vapor are discussed (Table 1).

Table 1 The results of color test of 4-aminoantipyrine with phenols and phenolic boiling point

Compound	b.p., ℃	R_1	R_2	R_3	R_4	R_5	R_6	Reaction[1]
Phenol	182	OH						3-S
o-Cresol	191	OH	CH₃					3-S
m-Cresol	202	OH		CH₃				3-S
p-Cresol	202	OH			CH₃			0
2,3-Dimethylphenol	218	OH	CH₃	CH₃				3-S
2,4-Dimehtylphenol	211	OH	CH₃		CH₃			0
2,5-Dimethylphenol	211.5	OH	CH₃			CH₃		3-S

Table 1 (Continued)

Compound	b.p., ℃	R_1	R_2	R_3	R_4	R_5	R_6	Reaction[1]
2,6-Dimethylphenol	212	OH	CH₃				CH₃	3-S
3,4-Dimethylphenol	225	OH		CH₃	CH₃			0
3,5-Dimethylphenol	219.5	OH		CH₃		CH₃		3-S[2]
o-Chlorophenol	175	OH	Cl					3-S
m-Chlorophenol	214	OH		Cl				3-S
p-Chlorophenol	217	OH			Cl			3-S
o-Nitrophenol	214.5	OH	NO₂					0
m-Nitrophenol	194	OH		NO₂				2-S
p-Nitrophenol	273	OH			NO₂			0
Catechol	245.5	OH	OH					3-Ins.
Resorcinol	280	OH		OH				3-Ins.
Hydroquinone	285	OH			OH			1-S
Pyrogallol	309	OH	OH	OH				3-Ins.
Pyloroglucinol		OH		OH		OH		3-Ins.

[1] The numbers refer to the strength of the test and the letters to the solubility of the colors in chloroform. Number 3 represents a strong test; 2, a moderate test; 1, a slight test; S, soluble; Ins. insoluble

[2] All positive tests produce varying shades of red except this one which is purple.

There are a lot of analytical methods for phenols, such as chemical analysis (NEPBC, 1989; GEUAMPS, 1983), chromatographic analysis (Yao, 1990), flow injection analysis (Frenzel, 1992; Yan, 1986; Trojanek, 1986; Chey, 1977; Armentrout, 1979; Shoup, 1982; Xu, 1994), electrochemical analysis (He, 1986; Lu, 1990), spectrometric analysis and so on. This paper only deals with the progress of optical determination for phenolic compounds. The important methods of optical determination for phenols in sewage are summed up in Table 2.

Table 2   The optical analytical methods of phenolic compounds

Classification of method	Name of method[1]	Pretreatment method[2]	Determined substance[3]	Linear range, mg/L	Detection limit, mg/L	Recovery, %	Water system
Visible spectrometry	4-AAP spectro.	Predist.	V.P.	0 – 5.0	0.1		Sewage
	4-AAP spectro.	Predist. saturated by NaCl	V.P.	0 – 5.5	0.05		Sewage
	4-AAP spectro. extracted by CHCl₃	Predist.	V.P.	0 – 0.12	0.002		Drinking water or surface water
	4-AAP spectro.	Extra.—reextra.	Phenols	0 – 1.3	0.04	95 – 101	Wastewater, river water
	MBTH spectro.	Predist.	V.P.	0 – 3.0	0.002	95 – 110	Sewage, surface water
	Berthelot reaction spectro.	Predist.	V.P.	0 – 1.0	0.05	94 – 103	Wastewater surface water

Table 2 (Continued)

Classification of method	Name of method[1]	Pretreatment method[2]	Determined substance[3]	Linear range, mg/L	Detection limit, mg/L	Recovery, %	Water system
UV-spectrometry	Three-length spectro.		Phenols	0 – 100	0.1	101 – 104	Turbid water
	UV-ratio method	Predist.	V. P.	0 – 5.5			Wastewater, surface water
	UV-spectro.	Extra. or concentration by resin	Phenols	0 – 110	0.001	89 – 98	Drinking water, surface water
	UV-spectro.	Extra. —reextra.	Phenols		0.002	~100	Drinking water, surface water
Derivative spectrophotometry	First-order		Phenols	0 – 100	0.04	98 – 102	Wastewater, surface water
	Forth-order		Phenols	0 – 140	0.1	94 – 110	idem.
	Forth-order	Extra. —reextra.	Phenols	0 – 10	0.005	92 – 105	Surfacewater, river water
	Higher-order	Predist. or centrifugal separation	Phenols	0 – 100	0.06	92 – 97	Wastewater
	Fluorescent spectro.	Predist. or extra.	Phenols and cresol	0 – 0.25	0.001	71 – 80	Nature water
	IR	Extra.	Phenols	12 – 10000	12		Phenolic solution and wastewater
	AAS	Precipatation and extra.	Phenols	0 – 0.023	0.001	98 – 112	Nature water

[1]Spectro. means spectrometry; 4-AAP is the abbreviation of 4-aminoantipyrine and MBTH is the abbreviation of 3-methyl-2-benzothiazoline hydrazone in the column;

[2] Predist. means predistillation; Extra. means extraction, and reextra. is reextraction in this column;
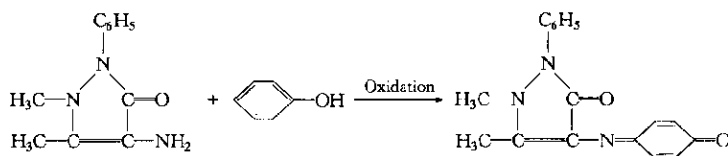
[3] V. P. means volatile phenols in this column.
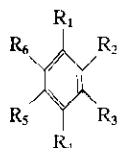
2　Spectrophotometric methods

Phosphotungstate and phosphomolybdate spectrophotometries which was proposed by Folin and his coworker (Folin, 1915) is the earliest optical determination methods for phenols in water and the 4-AAP (4-aminoantipyrine) spectrometry is the most common method which was first proposed and studied thoroughly by Elsenstaedt (Elsenstaedt, 1938; 1943). Now, 4-APP method has been used as National Standard Environmental Monitoring method by China and many other countries (Wei, 1990).

The 4-AAP method depends upon the purplish red color obtained on reacting 4-AAP with phenols in presence of potassium ferricyanide (oxidant) in the medium of basic buffer solution

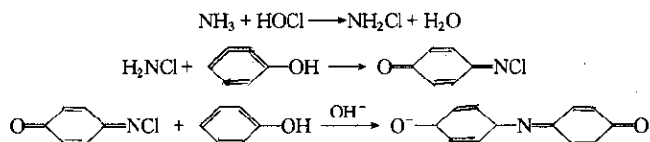$(NH_3\text{-}NH_4Cl, \ pH = 10.0 \pm 0.2)$. The reaction is:

Phenols in the range of 0.1—5.0 mg/L in sewage can be determined directly using spectrophotometer. The purplish red product can be extracted into $CHCl_3$. The sensitivity of the method is 50 times as many as directly spectrophotometry. The detection limit can be reduced to 0.002 mg/L. Elsenstaedt had studied the reactive limits of 69 phenols and 17 naphthols. Table 1 has listed the reactions of 21 common phenols with 4-AAP. The structural formula in Table 1 is based on
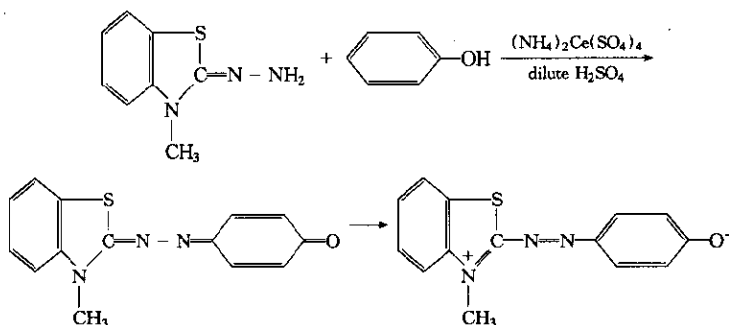

The conclusions drawn by Elsenstaedt (Elsenstaedt, 1943) are as follows: (1) There must be at least one free phenolic hydroxyl group in the molecule for a positive test. (2) Substituents in the para position to the hydroxyl group prevent the reaction except as follows: halogen, carboxyl, sulfonic acid, hydroxyl, and methoxyl. These groups are probably expelled. (3) A nitro group in the ortho position prevents reaction and a nitro group in the meta position inhibits the test but not completely. (4) Coupling of aminoantipyrine with the phenol takes place in the para position rather than in the ortho position. (5) When the para position is blocked by an alkyl, aryl, ester, nitro, benzoyl, nitroso, or aldehyde groups, no color reaction takes place even though the ortho positions are unsubstituted. In a word, phenols in sewage determined by 4-AAP method are phenolic compounds in which there is no substituent in the para position to the hydroxyl group except X, COOH, SO_3H, OH, OCH_3 group. Elsenstaedt's work showed when ammonium hydroxide is used in the medium of 4-AAP method there is a distinct positive test in the determination of phenols. Ochynski (Ochynski, 1960) recommended that potassium persulfate (or ammonium persulfate) was used as oxidant in 4-AAP method in order to prevent the color product faded. But most of the researchers use potassium hexacyanoferrate (III). Mohler (Mohler, 1957) summarized research references of predecessors, conclusion by comparison with other determination methods of phenols in sewage (e.g. Gibbs method-chlorimide dibromoquinone color developing, nitrosophenol method, IR and UV methods) is: 4-AAP method is the fastest, most accurate and precise one, and the reagents are stable, maximum absorption wavelengths of the purplish red dye and the color produced by 4-AAP coupling with phenols are almost the same. Deficiencies of the method are: there are the interference of aniline and keto-enol system coupling with 4-AAP, phenols substituted in the para position can not be determined, the sensitivity changes with the pH greatly, different phenolic compounds differ greatly in the intensity of color developing (Wei, 1990). Phenolic content determined by 4-AAP method is the total concentration of phenol and phenolic compounds coupling with 4-AAP while the concentration of phenolic compounds in sewage is lower. Ettinger

(Ettinger, 1948) studied the experimental conditions for determining phenols by 4-AAP method thoroughly. And the absorption capacity for the products of 4-AAP coupling with 7 common phenols was studied. λ_{max} of colored products to the solution is almost at 510 nm, and that of colored products extracted by chloroform is at 460 nm. The results studied by Ettinger are adopted by many nations as standard monitoring method (Wei, 1990). Another spectrophotometry for the determination of phenols is Berthelot's reaction spectrophotometry (Tao, 1983). Berthelot's reaction is as follows:

$$NH_3 + HOCl \longrightarrow NH_2Cl + H_2O$$

The reaction was first used for determining micro ammonia in water (Tetlow, 1964; Pym, 1976; Hampson, 1977; Crowther, 1980). The reaction is used for determining micro phenols in water by Tao (Tao, 1983). The procedure is that Jacob's method is used to prepare aminochloride as oxidative reagent for color developing, sodium nitroprussiate is used as catalyst, and phenols in sewage, in which interfering materials are removed by acidity predistillation, react with aminochloride and produce emerald green indigo phenol. Molar absorption coefficients of products at the wavelength of 680 nm for phenol, o-methyl phenol, salicylic acid, metadioxybenzene, α-naphthol are 2.0, 1.8, 1.2, 0.74, 0.70 ($\times 10^{-4}$), respectively. 0.005—1 mg/L volatile phenols can be determined by using this method. Hünig (Hünig, 1957) first advanced that phenols were determined by using MBTH (3-methyl-2-benzothiazolylzone) as color developing reagent. The reaction is as follows:

Kamata (Kamata, 1966) applied the above-mentioned method to determine the phenolic derivatives. Umeda (Umeda, 1963) used it to analysising phenol. The application of the method is restricted because this method is not verified with others. Then, this method is used for determining phenols in Flow Injection Analysis (FIA) (Friestad, 1969). The procedure is: after 5 min when phenols in sewage reaction with MBTH solution in coloring tube, solution of cerium sulfate is added as the oxidant, the content of volatile phenols is determined at the wavelength of 520 nm in the medium of neutral buffer solution made up with NaOH, EDTA and H_3BO_3, while the color developing time is 15 min. The detection limit of the method is 0.01 mg/L. The sensitivity of the method is 10 times of the 4-AAP method (the detection limit of 4-AAP method is 0.1 mg/L). Friestad studied the sensitivity and λ_{max} for the determination of 32 phenols by using

MBTH method and checked it by using 4-AAP method (Table 3).

Table 3   Molar absorptive values of phenolic compound

| Compound | | | Reaction product | |
| Name | Molar weight | λ_{max} | Apparent molar absorptivity, $\times 10^{-3}$ | |
			MBTH method	4-AAP method
Phenol	94.1	520	26	14
2-Cresol	108.1	500	24	14
3-Cresol	108.1	510	23	9
4-Cresol	108.1	550	9	N
4-Chlorophenol	128.6	520	22	9
4-Bromophenol	173.0	520	23	11
3-Iodophenol	220.0	530	28	19
3-Aminophenol	109.1	460	19	12
4-Aminophenol	109.1	500	10	N
2-Nitrophenol	139.1	550	14	7
3-Nitrophenol	139.1	520	20	5
4-Nitrophenol	139.1	500	2	N
4-Hydroxybenzoic acid	138.1	525	18	13
4-Methylthiophenol	140.2	520	20	15
2, 4-Dichlorophenol	163.0	530	28	22
2, 4-Dibromophenol	251.9	530	36	30
2, 6-Dibromophenol	251.9	470	23	29
4-Chlororesorcinol	142.6	475	27	15
3-Methyl-4-methylthio-phenol	154.2	500	13	16
2, 4-Dinitrophenol	184.1	N	N	N
2, 4, 5-Trichlorophenol	197.5	520	16	23
2, 5-Dichloro-4-bromophenol	241.9	535	20	19
2, 5-Dichloro-4-iodophenol	288.9	530	20	22
2, 6-Diiodo-4-cyanophenol	370.9	N	N	N
2, 4-Dihydroxy benzophenone	214.2	475	23	N
4, 4'-Dihydroxy benzophenone	214.2	595	11	N
2-Cyclohexylphenol	176.3	505	24	14
4-Cyclohexylphenol	176.3	540	16	N
2-Phenylphenol	170.2	520	30	18
4-Phenylphenol	170.2	580	13	N
1-Naphthol	144.2	510	11	9
2-Naphthol	144.2	510	19	9

Note: N means no reaction

Goulden (Goulden, 1973) has improved MBTH spectrophotometry. Use KOH-NaH_2PO_4-H_3BO_4 as the buffer solution and the color products are extracted by chloroform with 100%

extraction ratio. There is no obvious difference between the MBTH method and 4-AAP method in the determination of water samples. The detection limit of phenols by Goulden's method is 0.002 mg/L.

Lei Zhifang(Lei, 1974) *et al*. studied spectrophotometric method for determining phenol and parachlorophenol by using MBTH as color developing reagent. The buffer solution is the equal volume mixture of NaOH-EDTA-H_3BO_3 and alcohol. The sensitivity for the determination of phenols in water samples is improved obviously. Besides oxidative coupling with phenols, MBTH can react with methylene compounds and aromatic amine. Most of interferences can be removed when basic buffer of EDTA-H_3BO_3 is used. Interferences of S^{2-} and aromatic amine can be removed by using predistillation in acid medium and in the presence of $CuSO_4$, but interferences of $Cr_2O_7^{2-}$ and formaldehyde over 50 mg/L, I^- and Fe^{2+} over 150 mg/L can not be removed. Frenzel (Frenzel, 1992) had used MBTH spectrophotometry for determining phenolic compounds in FIA.

3   UV spectrum methods

3.1   UV spectrophotometry

Based on the variation of UV spectrum for phenolic compounds with alkalinity of medium, Murray (Murray, 1949) studied UV spectrophotometry for determining phenols in gasoline; Schmauch (Schmauch, 1954) studied the determination of phenols in sewage by using UV spectrophotometry. Smullin (Smullin, 1955) and Englis (Englis, 1957) determined the contents of phenols in surface active agent and foods. The above-mentioned methods are based on λ_{max} red shift (Coggeshall, 1949; Doub, 1974) of UV spectrum of phenols in basic medium, the difference between the absorbance of phenols in basic solution and in neutral solution is used for determining phenols (Authur, 1963). James (James, 1982) determined the content of phenols at the maximum wavelength ($\sim$ 291 nm) of UV-spectrum of negative phenolic ions. Based on the difference of absorbance at the wavelength of 291 nm between phenolic negative ion and phenol, Fountaine (Fountaine, 1974) designed a new instrument in which Two Hollow Cathode Lamps are used as light source. Fountaine determined phenols in water sample with this instrument. In this instrument, the first lamp is used to determining the variation (or difference) of absorbance of transformation from phenols into phenolate ions at the wavelength of 291 nm by adding NaOH, and the second lamp is used to determining the absorbance difference (noise difference) produced by the drift of datum line at the wavelength of 350 nm. The net difference between the variation of absorbance at 291 nm and that of the drift of datum line is used to determining phenols. James (James, 1981) manufactured above-mentioned instrument, and put it on the market. Conditions of the instrument using for determining phenols are there is no absorption of light at 291 nm in pH = 7, and there are no substances absorbing light at the wavelength of 291 nm in water sample, and there is no interfering in pH = 12. If above-mentioned conditions are satisfied the determination of 0—100 mg/L phenols is according with Lamber-Beer law. Mohler (Mohler, 1957) proposed UV Ratio method to determining phenols. The method is used as quantitative analysis of phenols by using relations between absorbance ratios of phenolates in basic solution and phenols in neutral

solution at the same wavelength and phenolic concentrations. Norwitz (Norwitz, 1979), Afghan (Afghan, 1974) and Farino (Farino, 1981) *et al.* studied the determining conditions of UV-Ratio method in detail. They had studied 36 phenolic compounds and found: 28 phenols could be determined and recoveries of the phenols were from 0 (there are 8 phenolic compounds) to 148% (picric acid), in which the recovery below 5% for phenolic compound is only one (salicylic acid), when the phenolic content is calculated according to phenol. If predistillation is used recoveries of phenols are from 0 (there are 7 phenolic compounds) to 110% (*o*-cresol, *o*-chlorophenol). 29 phenols can be determined in 32 phenols distilled out from wastewater by UV-Ratio method and the recoveries of 7 of determined phenols are below 5%. Therefore, the volatile phenols determined by UV-Ratio method containing 22 phenolic compounds

Wang Lili (Wang, 1988) had studied concentration and UV- spectrophotometry for phenols. First, phenols are concentrated by using micro-resin (GDX-52), then the phenols in the resin are washed down by using NaOH solution and the content of phenols is determined at the wavelength of 291 nm. The selectivity of the method is better and most of the interference of organic compounds can be removed.

Shi Mingshui (Shi, 1980) had studied a method in which using ether-chloroform (1:1) as extractant and 0.1 mol/L NaOH solution as reextractant, the contents of phenols in water samples can be obtained by using the absorbance differences between phenolate and phenol in different acidity at 235 nm or 290 nm. Cheng Rongming (Cheng, 1988) proposed an analytical method of phenols in turbid water by using UV three-wavelength spectrometry, and used it for determining phenolic content in turbid river water, seawater, lake water and so on.

3.2 UV-derivative spectrophotometry (UVDS)

Talsky (Talsky, 1983) reviewed an important application of High-Order Derivative Spectrum (HODS) in environmental analysis. Phenols and anilines in wastewater can be determined simultaneously by using HODS. Chen Shuyu (Chen, 1986) studied an experimental method of derivative by which micro phenols in wastewater can be determined. An instrument and its parameter are defind. According to above-mentioned method, linear range of phenolic determination is 0—100 mg/L, the detection limit is 0.06 mg/L, and recoveries of phenols in standard addition method are 92%—97%. Wang Lin (Wang, 1990) studied the determination of phenolic compounds in oil refining wastewater by UV-4th order derivative spectrum (4-ODS) in the medium of 1 mol/L HCl solution. Li Ping (Li, 1994) studied a simultaneous determining method for phenol and aniline with 1st order derivative spectrum. The method is that pH of water sample is adjusted to 5—9 in order to determine phenol and aniline directly. It is simple and time saving. Wu Guoqiang (Wu, 1986) studied a method for phenols determined by 4-ODS directly in waste water adjusted acidity with H_2SO_4 solution. Yuan Cunguang *et al.* (Yuan, 1993; 1994; Liu, 1995) studied thoroughly an analytical method for phenols and aromatic amines in oil field wastewater with 4-ODS. The method is: water sample containing phenols over 0.1 mg/L and anilines over 0.08 mg/L is took into a volumetric flask, adjust its pH to 2.5 with hydrochloric acid, draw up its 4-ODS, then the content of phenols is obtained by using peak-peak method at 272 nm and 276 nm and that of anilines is determined by using peak-zero method at 204 nm.

Interferences of common pollutant can be removed in this method. After significance test, both of the precision and accuracy of the method are better than 4-AAP method. There is no significance variation in determining results of phenols in wastewater samples between 4-ODS and 4-AAP method, 4-ODS method (Yuan, 1993) can eliminate the stapes of pretreatment, distillation and color developing. In order to improve the sensitivity of determining phenols further, Yuan Cunguang *et al*. studied an analytical method of determining micro phenol in water by using *n*-butyl acetate or isoamyl acetate as extractant and 5% NaOH solution as reextractant. This method reduces the detective limit to 0.005 mg/L.

4   Other optical analysis methods

Xie Chongge (Xie, 1985) studied a fast analytical method for phenols in nature water by fluorescence spectrophotometry. The procedure is: extracting and concentrating phenol and cresol from water sample with *n*-butyl acetate, then reextracting phenols from organic phase with 1.6 mol/L NaOH solution. Reextractive solution is acidified to pH 1—3. Use ultraviolet light of wavelength of 265 nm or 275 nm as excitating light. Determine phenolic content in the water sample with fluorescence at the peak wavelength of 301 nm. The detective limit of this method is 0.005 mg/L. Wang Xiaomin (Wang, 1986) proposed that *n*-butanol is used as extractant of phenols from wastewater, and the organic phase is determined directly with fluorescence spectrophotometry. The excitating wavelength is at 269 nm, and the determining wavelength of fluorescence is at 298 nm. Phenol, *o*-cresol, *p*-chlorophenol, trichlorophenol, pentachlorophenol (PCP) *etc*. can be determined simultaneously, and other phenolic compounds, aniline and benzol do not interfere for determining phenols.

Simard (Simard, 1951) and Zhang Liqun (Zhang, 1991) proposed an infrared absorptive spectroscopy method by which phenol over 10 mg/L in water sample and wastewater can be determined. Phenols in water are extracted with chloroform, water is removed from organic phase with absorptive tube. Organic phase is pour into stationary absorptive cell with a microliter syringe. Infrared absorbance is determined at 1595 cm^{-1}. Then, phenolic content is obtained according to Lambert-Beer law. Linear range of the method is 12-10000 mg/L.

Yamamoto (Yamamoto, 1965) found if there were excessive ferric tri-1, 10-phenanthroline-ferrous complex cation, pentachlorophenol (PCP) could form chelate compound with this cation, which could be extracted by nitrobenzene. The composition of extracted compound is $[Fe(1, 10$-phenanthroline-ferrous$)_3]$ $(C_6Cl_5O)_2$. Yamamoto (Yamamoto, 1967) studied atomic absorption spectrophotometry (AAS) for PCP: solution extracted by nitrobenzene is sprayed, ferrum is determined with ferro-hollow cathod lamp, and PCP is indirectly determined. Mitsui (Mitsui, 1974) studied AAS method for phenol: phenol is nitrated into nitrophenol in the presence of sodium cobaltinitrite, and nitrophenol reacts further with Co^{3+} to produce cobaltic nitrophenol complex. The complex can be extracted by methyl isobutyl ketone (MIBK), and the organic phase is sprayed to burn. So the phenolic content is obtained indirectly by cobaltic content determined by AAS method. Xu Boxing (Xu, 1985) studied a method: phenol in water is bromated to bromol,

excessive bromine reacts with I^- to produce I_2, product (I_2) is extracted by cyclohexane. I_2 in organic phase is reduced to I^-, then I^- reacts with Cd^{3+} to produce H_2CdI_4 in the medium of sulfate acid. H_2CdI_4 is extracted into organic phase by MIBK. Organic phase is sprayed directly, and the content of Cd is determined by air-acetylene flame AAS method. Then, the content of phenols is indirectly obtained. Phenols determined by the method include: phenol, o-chlorophenol, p-chlorophenol, o-cresol, m-cresol, the bromating ratios are 100, 46, 35, 87, 108 (%), respectively. Because bromine can react with some organic compound, such as unsaturated organic acid and anilines which make the determinate error. These compounds must be concealed. The procedure is: phenols are extracted by 1:1 chloroform-ether in the medium of pH 8—9 and reextracted by 0.1 mol/L KOH solution. Then the content of phenols is determined according to the method above-mentioned.

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