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SIMPLE AND RAPID SPECTROPHOTOMETRIC METHOD FOR PHENOL DETERMINATION IN AQUEOUS MEDIA

BY

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Abstract. Simple and selective determination of phenol from aqueous media was spectrophotometrically examined using ferric chloride as colour reagent. The reaction between phenol and $FeCl_3$ occurs rapidly (1-2 min), without to be necessary the adjustment of solution pH. The visible spectra of the purple complex, recorded against distilled water, show a maximum at 540 nm, and the absorbance remains stable for at least 10 hours. This method allows the determination of phenol from aqueous media in a relatively wide concentration range (0.09 – 2.30 $mg \cdot mL^{-1}$), with acceptable detection limits. The interferences caused by methanol, ethanol, acetone and ethylic ether were evaluated on the basis of the selectivity coefficients. The validation of the proposed method was done by recovery tests of phenol in tap water. Experimental results indicate that the proposed method allows a rapid and simple quantitative determination of phenol in aqueous media, and can be used to test the quality of industrial effluents.

Keywords: Phenol; ferric chloride; spectrophotometric method; aqueous solution; industrial applications.

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1. Introduction

The pollution of environment due to the industrial activities is an actual issue worldwide. Whether it's metal ions or organic compounds, the presence of pollutants in the environment has serious negative consequences on the quality of ecosystems and human health (Akunwa *et al*., 2014). Industrial effluents are recognized as one of the most important sources of environmental pollution. This is why the monitoring of the pollutant content of these effluents is essential in order to be able to select the most efficient treatment method before being discharged into the environment. But, the monitoring of industrial effluents requires the use of simple, rapid and inexpensive analysis methods, even if the analytical performances of these are not always excellent. Therefore, the development of such analysis methods is still a current direction of research.

The presence of phenols in natural or drinking water is often due to industrial contamination. The wastewater resulted from various industrial activities, such as chemical industry, paper and pulp industry, petrochemical industry, etc., frequently contains relatively high concentrations of phenol (Gonzalez-Garcia *et al*., 2001; Iniesta *et al*., 2002; Cordova Villegas *et al*., 2016). Various and serious diseases, (ex. neurologic, cardiac, respiratory, renal and digestive) (Tisler and Zagorc-Koncan, 1997) are caused by the increased concentration of phenol in human organism, due to the incomplete treatment of the industrial effluents discharged into environment. Therefore, the simple and rapid analysis of phenol is still considered important, since the maximum permissible limit of this pollutant in industrial effluents becomes progressively low (Directive 2000/60/EC, 2000).

Many liquid- or gas-chromatographic techniques and electrochemical techniques (Brega *et al*., 1990; Zhao and Lee, 2001; Pilar Vinas *et al*., 2006; Wang *et al*., 2006; Vidal *et al*., 2008; Beitollahi *et al*., 2014) have been development for the selective and sensitive analysis of phenol in aqueous media, from different types of samples. Even if their analytical performances are very good (low detection limit, high selectivity and accuracy, etc.), are inappropriate for the analysis of phenol in industrial laboratories, due to high cost of analyzes, multi-step and laborious sampling procedures, long work time, expensive equipments, etc.

Unlike these, the VIS molecular absorption spectrometry is more appropriate for the development of simple, rapid and inexpensive analytical method for the quantitative determination of phenol from aqueous media (Fiamegos *et al*., 2000; Gonzalez *et al*., 2003). This is because the spectrophotometric methods are based on the formation of a coloured phenol compound that absorbs radiation at a certain wavelength (Bulgariu, 2011). Due to their simplicity, short work time, adaptability at various experimental conditions, accuracy, inexpensive equipments, etc., (Christian, 1994; Dean, 1995), the spectrophotometric methods are more suitable for industrial laboratory use. However, all these advantages of spectrophotometric methods are valid only if the colour reagent (which is necessary to obtain the coloured phenol compound) is also cheap and stable over time. If the colour reagent is expensive and has a low stability, additional precautions should be taken, which limits the applicability of the spectrophotometric methods in industrial laboratories.

In this study a simple and rapid spectrophotometric method for phenol determination in aqueous media was examined, using ferric chloride as colour reagent. The colour reagent selection was made taking into account all of the above mentioned observations. The analytical performances of the proposed spectrophotometric method were determined on the basis of experimental results. The interferences caused by methanol, ethanol, acetone and ethylic ether were evaluated on the basis of the selectivity coefficients. The validation of phenol determination through this method was done by recovery test using tap water samples.

2. Experimental

2.1. Materials

All the chemical reagents (phenol, $FeCl_3$, methanol, ethanol, acetone, ethylic ether) used in the experiments were of analytical reagents degree and were used without supplementary purifications. The stock solution of phenol (10^{-1} mol·L^{-1}) was prepared by dissolving a certain amount of solid phenol in distilled water. The working solutions were prepared by dilution from the stock solution with distilled water. The ferric chloride solution was obtained by dissolving 1.61 g of solid $FeCl_3$ in 100 mL of distilled water. One drop of HCl solution (36%) was added to the ferric chloride solution, before diluting it to the appropriate volume, to prevent the secondary hydrolysis. Spectrophotometric measurements were performed with VIS Spectrophotometer model YA1407020, in 1.0 cm glass cells, at room temperature.

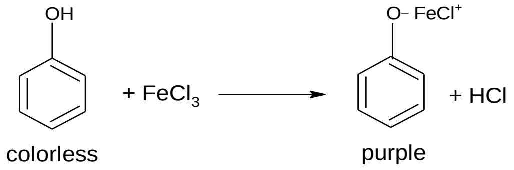
2.2. Analytical Procedure

Volumes of 0.5 – 4.0 mL of phenol solution (9.41 mg·mL^{-1}) were transferred into 25 mL volumetric flasks. The measured solutions were diluted with around 10 mL of distilled water, and after homogenization 1.0 mL of $FeCl_3$ solution were added. The solutions were diluted to the mark with distilled water and mix. The absorbance of each solution was measured in wavelength domain between 470 – 700 nm, against distilled water. The phenol concentration in unknown samples was determined using a prepared calibration graph, obtained by graphical representation of the absorbance (measured at 540 nm) in function of phenol concentration from etalon solutions. The selectivity coefficients were calculated for each case, as ratio between the phenol concentration and interfering compound concentration which gives a 5% change of absorbance in a reference solution (Christian, 1994). The recovery test was done using tap water samples from laboratories of our Faculty, where the phenol concentration was adjusted to certain values with the stock solution.

3. Results and Discussions

3.1. Determination of Qualitative Parameters

The proposed method for phenol determination is based on the reaction between phenol and ferric chloride in aqueous media, when a soluble purple reaction product is obtained, according to the equation:



(1)

This reaction was first used for the qualitative identification of phenol (Ripan *et al.*, 1963), when it was observed that the purple colour appears only for phenol, while the cresols give different colorations. The different coloration of compounds from phenol series in presence of $FeCl_3$ suggests a possible selectivity, and this was the basis for selecting this reaction for the quantitative determination of phenol using a spectrophotometric method.

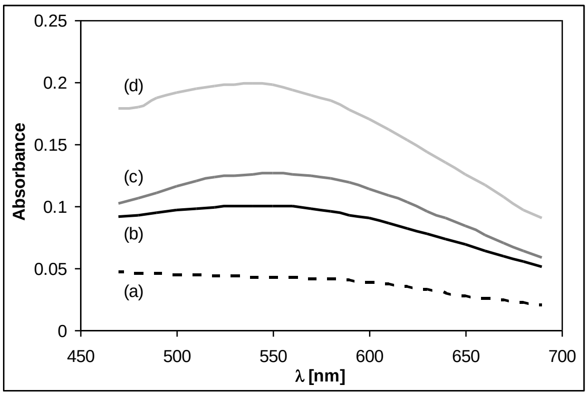


Fig. 1 − Absorption spectra recorded for purple complex formed between phenol and ferric chloride, against distilled water
((a): 0.09 mg·mL; (b): 0.37 mg·mL; (c): 0.75 mg·mL; (d): 1.13 mg·mL).

In order to determine the qualitative characteristics of purple complex formed between phenol and $FeCl_3$, the VIS absorption spectra were recorded in 470 – 700 nm, against distilled water, for different concentration of phenol, and are illustrated in Fig. 1.

It can be observed form Fig. 1 that the purple complex has a maximum of absorption at 540 nm, for all phenol concentrations, and this value was considered as λ_{max} and was used for quantitative determinations. In addition, the values of other qualitative parameters (spectral bandwidth ($\Delta\lambda_{1/2}$) and molar absorption coefficient (ε)) do not also depend on the concentration of the phenol in the solution, and their mean values are $\Delta\lambda_{1/2}$ = 186 nm and $\varepsilon = 1.19\text{x}10^3\ \text{L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$. Therefore, from a qualitative point of view, the colour reaction between phenol and ferric chloride fulfills all the conditions and can be used for the quantitative determination of phenol by a spectrophotometric method.

3.2. Quantitative Analysis of Phenol

In order to check the applicability of this colour reaction for the quantitative determination of phenol in aqueous solution, the calibration curve was constructed using seven etalon solutions, as was described in the Experimental section. For each solution, the absorbance was measured against distilled water at 540 nm (considered maximum absorption wavelength), and the obtained calibration curve is presented in Fig. 2.

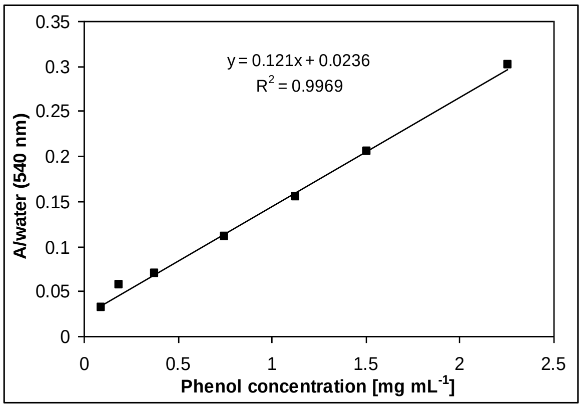


Fig. 2 – Calibration curves obtained in case of spectrophotometric determination of phenol with ferric chloride.

The most important quantitative parameters of the spectrophotometric determination of phenol with ferric chloride are summarized in Table 1. As can be observed from Table 1, the spectrophotometric determination of phenol with $FeCl_3$ has reasonable linear concentration range, high sensitivity and accuracy, and requires a short working time. All these characteristics make this method suitable for use in industrial laboratories.

The effect of possible interfering organic compounds has been evaluated using selectivity coefficients ($a_{phenol,\ j}$), defined as the ratio between phenol concentration (C_{phenol}, $mg \cdot mL^{-1}$) and interfering compound concentration (C_j, $mg \cdot mL^{-1}$) which cause a change in measured absorbance of 5% in a reference solution.

Table 1

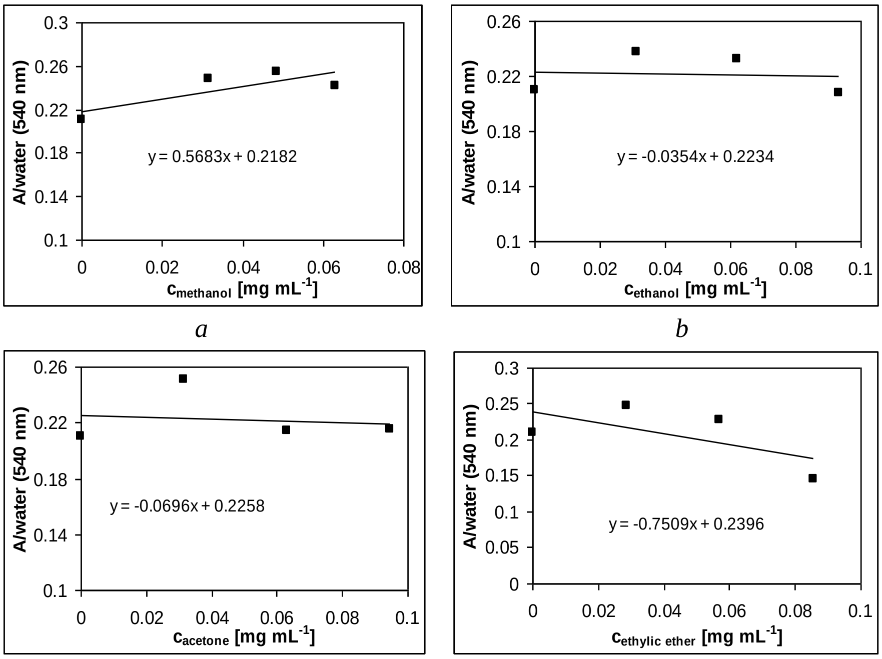
Quantitative Parameters for Spectrophotometric Determination of Phenol with $FeCl_3$

Parameter	Obtained value
λ_{max}, [nm]	540
Time of color appearance, [min]	1-2
Linear concentration range, [$mg \cdot mL^{-1}$]	0.09 – 2.30
Regression coefficient	0.9969
Calibration sensitivity, [$mL \cdot mg^{-1}$]	0.121
Limit of detection, [$mg \cdot mL^{-1}$]	0.060
RDS, [%]	1.16

In this study, a phenol solution of 0.37 $mg \cdot mL^{-1}$ was used as the reference solution, and the interfering compounds were methanol, ethanol, acetone and ethyl ether. Selection of interfering compounds was made considering their chemical similarities with phenol and their abundance in industrial effluents. In Fig. 3 are presented the experimental results obtained for each interfering compound, and the values of selectivity coefficients, calculated from regression equations (inside Fig. 3), are summarized in Table 2.

The obtained values of selectivity coefficients indicate that the proposed method is selective for phenol in the presence of some other organic compounds that are relatively abundant in the industrial effluents. Thus, the concentration of methanol and ethylic ether may be 100 times larger than the phenol concentration to change the absorbance with 5%. Hence it can be considered that these compounds do not interfere in the spectrophotometric determination of phenol using ferric chloride as colour reagent. For acetone, the concentration up to which the change of absorption is below 5% may be up to 10 times higher than the phenol concentration, while an ethanol concentration up to 1.25 times greater does not influence the spectrophotometric determination of phenol by the method proposed.

However, in industrial effluents besides some organic compounds (such as methanol, ethanol, acetone or ethylic ether) which may come from technological processes, the main constituents of water (inorganic anions and cations, soluble salts, etc.), are also present in high concentrations. Therefore, the influence of these chemical species present in the real water samples, on the spectrophotometric determination of phenol by this method should be also examined. This was done through recovery tests, using tap water from the laboratories of our faculty. Thus, 10 mL of tap water was transferred in a series of 25 mL volumetric flasks, and 0.5, 1.0, 1.5 and 2.0 mL of phenol stock solution was added immediately. After the addition of 1.0 mL of $FeCl_3$ solution, the volumetric flasks were diluted to the mark with distilled water, and analyzed according with the procedure described in Experimental section.



a *b*

c *d*

Fig. 3 – Measured absorbance values for different concentrations of interfering compounds: *a* – methanol; *b* – ethanol; *c* – acetone; *d* – ethylic ether.

Table 2

The Selectivity Coefficients

Interfering compound	C_{phenol}, [mg·mL^{-1}]	C_j, [mg·mL^{-1}]	log $a_{phenol,\, j}$
Methanol	0.376	0.009	-2.046
Ethanol	0.376	0.158	-0.801
Acetone	0.376	0.079	-1.102
Ethylic ether	0.376	0.007	-2.155

The phenol concentration in each sample was determined using the regression equation of the prepared calibration graph. The mean values of recovery percents obtained for each phenol concentration added in the tap water samples are presented in Table 3. A good agreement between the concentration of phenol added to tap water and determined from the calibration curve was obtained for all analyzed samples.

Table 3

Experimental Values of Recovery Tests

No.	$V_{tap\ water}$ [mL]	C_{phenol}^{added} [mg·mL^{-1}]	C_{phenol}^{found} [mg·mL^{-1}]	Recovered [%]
1.	10.0	0.189	0.184	97.35
2.	10.0	0.376	0.368	97.87
3.	10.0	0.565	0.559	98.94
4.	10.0	0.753	0.768	101.99

Therefore, the proposed method may be a good alternative for the determination of phenol from aqueous media and, due to its simplicity, rapidity and low cost, can have many uses in industrial laboratories.

4. Conclusions

The proposed spectrophotometric method using ferric chloride as a colour reagent for quantitative determination of phenol from aqueous media is simple, selective and precise, and requires a short working time. The purple reaction product is formed immediately, does not require the adjustment of solution pH and its absorbance (measured at 540 nm against distilled water) remains stable for at least 10 hours. The method allows the determination of phenol over the range 0.09 – 2.30 mg·mL^{-1}, with a molar absorption coefficient of 1.19x10^{3} L·mol^{-1}·cm^{-1}, and a detection limit of 0.06 mg·mL^{-1}. The good selectivity of the proposed method to phenol in the presence of some organic compounds (methanol, ethanol, acetone and ethylic ether) and of the main constituents of real water samples, indicate the possible utility of this methods in the phenol determination from aqueous media. Also, due to its simplicity, rapidity and low cost, this method can be successfully used in industrial laboratories.

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⁂ Directive 2000/60/EC, Council Directive 2000/60/EC of the European Parliament and of the Council Establishing a Framework for Community Action in the Field of Water Policy, Official Journal European Communities, L327/1.

METODĂ SPECTROFOTOMETRICĂ SIMPLĂ ŞI RAPIDĂ PENTRU DETERMINAREA FENOLULUI DIN MEDII APOASE

(Rezumat)

Determinarea simplă şi selectivă a fenolului din mediile apoase a fost examinată spectrofotometric folosind clorura ferică ca şi reactiv de culoare. Reacția dintre fenol și $FeCl_3$ are loc rapid (1-2 minute) şi nu necesită ajustarea pH-ul soluției apoase. Spectrele în domeniul VIS ale complexului violet, înregistrate faţă de apă distilată prezintă un maxim de absorbţie la 540 nm, iar absorbanţa rămâne stabilă timp cel puțin 10 ore. Această metodă permite determinarea fenolului din medii apoase într-un domeniu de concentrație relativ larg (0,1 - 2,3 $\text{mg}\cdot\text{mL}^{-1}$), cu o limită de detecţie acceptabilă. Interferențele cauzate de metanol, etanol, acetonă și eter etilic au fost evaluate pe baza coeficienților de selectivitate. Validarea metodei propuse a fost făcută prin teste de recuperare a fenolului în apa de la robinet. Rezultatele experimentale indică faptul că metoda propusă permite o determinare cantitativă rapidă și simplă a fenolului din medii apoase și poate fi utilizată cu succes pentru a testa calitatea efluenților industriali.