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Determination of phenol, resorcinol and hydroquinone in air samples by synchronous fluorescence using partial least-squares (PLS)

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Abstract

The determination of phenolic compounds is of great importance owing to their high toxicity. Some of them are present in tobacco smoke and it is important for their monitoring in air of closed room. A simple, rapid and sensitive method was developed for simultaneous determination of hydroquinone, resorcinol and phenol in this kind of samples. Synchronous fluorescence technique was used and the data were processed by using the partial least-squares (PLS) chemometric algorithm. The concentrations for experimental calibration matrix were varied between 0.02 and 0.2 mg L^{-1} for hydroquinone, between 0.05 and 0.6 mg L^{-1} for resorcinol and between 0.05 and 0.4 mg L^{-1} for phenol in accordance with the national legislation. The cross-validation method was used to select the number of factors. To check the accuracy of the proposed method a recovery study on real samples was carried out.

Keywords: Hydroquinone; Resorcinol; Phenol; Synchronous fluorescence; PLS; Air samples

1. Introduction

Phenols are defined as hydroxyl derivates of benzene. The determination of these compounds is of interest in many fields, such as environmental control [1], neurochemistry [2,3] and pharmaceutical [4]. Moreover, some of them are formed from the pyrolisys of tobacco during the smoking process [5] and this is another source of pollution, particularly in closed room where smoking is allowed. These compounds have co-carcinogenic activity [6]. Hydroquinone causes severe effects on the central nervous system and together with resorcinol it is carcinogenic [7]. Phenol is considered to be very toxic to humans through oral exposure. Thus, the ingestion of 1 g of this compound has been reported as lethal with symptoms including muscle weakness and tremors, loss of coordination, paralysis, convulsions, coma and respiratory arrest [8]. All of these kinds of compounds are irritant [7]. So, the importance of monitoring phenols in air of closed room where smoking is allowed, such as offices, workshops, restaurants, etc. is to determine the concentration level of these harmful compounds owing to their toxicity and persistence in the environment.

The national legislation [9] suggests for hydroquinone, resorcinol and phenol: 4, 90 and 38 mg m^{-3} of air, respectively, for exposure time of 15 min.

There are several methods to determine these kind of phenols, with spectrometric detection and continuous flow [10], chromatography with different detectors [11–13], but only a few papers have been reported in air samples [14–16]. Although, these methods involved a previous step where the physical or chemical separation had to be made. Usually, the sample treatment is a laborious task and also, a long time consuming procedure is required to reach the complete extraction of dihydroxybenzenes derivates. Thus, the development of new methods, which makes possible the simultaneous determination of these compounds without any previous separations, is a relevant research subject.

Synchronous fluorescence is known as a useful technique to carry out simultaneous determinations of multicomponent samples without any pre-treatment. Moreover, the application of

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chemometric techniques as PCR, PLS1 and PLS2 to the fluorescence spectral data is being used for the analysis of complex mixtures [17–19] with the advantage that no need of prior separation or sample pre-treatment.

In the present paper, we propose a new method to determine phenol, hydroquinone and resorcinol in air samples by applying synchronous fluorescence and the robust multivariate calibration analysis (PLS1). One of the advantages of this method is that the analysis was carried out directly in air samples and the sample can be collected in a simple way.

2. Experimental

2.1. Apparatus

A computer-controlled spectrofluorimeter SLM Aminco Bowman serie 2, equipped with a xenon discharge light source (1500 W) was used to obtain all the spectra. Wavelength accuracy and wavelength repeatability were ±0.5 and ±0.25 nm, respectively. The excitation and emission slits can be varied from 2 to 16 nm and the selected were 8 nm. Fluorescence measurements were performed using a standard 1 cm × 1 cm quartz cell.

The spectra were saved in ASCII format, and transferred to PC Pentium II for subsequent manipulation that was carried out by applying Mathlab program an MVC1 subroutine [20].

2.2. Reagents

All reagents were of analytical grade and ultra pure water (18 MΩ) was used. Hydroquinone, resorcinol and phenol stock solutions were prepared daily by dissolving 0.0100 g of each analyte (Mallinckrodt) in 100 mL of water. The standard solutions were prepared by appropriate dilutions of each stock solution.

2.3. Sampling equipment

Absorption borosilicate glass bottles, of the Dreschel type, were used. There were equipped with interchangeable ground glass joints. The capacity of the bottles was 250 mL. The external diameter of the entry an exit tubes of the absorption bottles was 10 mm. The tube leading the air into the solution has an internal diameter of 8 mm and was 15 mm from the bottom of the bottle. The absorption bottle was connected to a pump that operated at a constant flow rate of 80 mL min^{-1}.

2.4. Sampling technique

The sampling was carried out in a room of 10 m^2 in which smoking was allowed. In order to assess the short exposure of 15 min, this time was established as a sampling time. A suitable volume of the absorption solution (25 mL of water) was placed in the absorption bottles and then connected to the pump. The sampling was performed at the same hour in different days and also at different hours in the same day.

3. Results and discussion

3.1. Solvent selection

The absorption solution for the extraction of analytes from the air samples was selected taking into account the solubility of them in different solvents, and also the fluorescence signals obtained in these solvents. The results showed that water was the most suitable solvent and by this way, a liquid–liquid extraction with organic solvent was avoided [14].

3.2. Selection of spectral feature

Hydroquinone, resorcinol and phenol in aqueous solution show native fluorescence (Fig. 1), the overlapping spectra prevented the direct determination of the analytes in the samples. So, synchronous fluorescence was used in order to reduce this overlapping. By this way, mixtures of hydroquinone and resorcinol can be resolved [14] but when a third component was present (phenol), the resolution of the new mixture was impossible because the resorcinol signal was overlapped to the phenol signal. PLS1 method allowed the resolution of the three components in the mixtures.

When synchronous fluorescence technique is used, the selection of wavelength interval is one of the most important experimental parameter. This selection was made empirically by considering the excitation and emission maxima for the three analytes and the scans were recorder from $\Delta\lambda = 5$ to 40 nm. For $\Delta\lambda \leq 10$ nm, the peaks could not be suitable separated. For $\Delta\lambda \geq 20$ nm, the fluorescence intensity decreased. For $\Delta\lambda = 15$ nm, the peaks showed a good shape with a synchronous scanning between $\lambda_{exc} = 230$–360 nm and $\lambda_{em} = 245$–375 nm. These selected spectral regions have 130 wavelength values for each mixture that were used in the multivariate analysis.

3.3. Calibration and test sets for multivariate analysis

A full factorial design was used to obtain the calibration set. A training set of nine standard solutions was prepared and

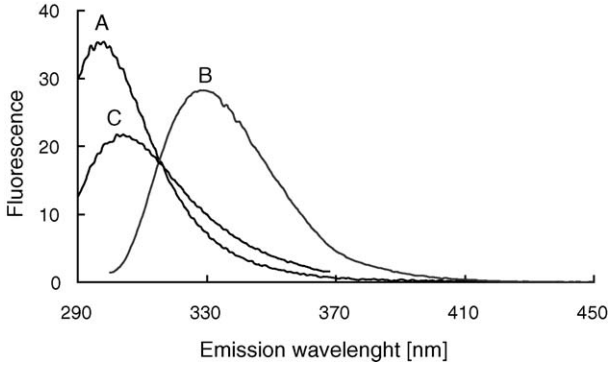

Fig. 1. Fluorescence spectra of: (A) phenol ($\lambda_{exc} = 272$ nm, $\lambda_{em} = 298$ nm); (B) hydroquinone ($\lambda_{exc} = 292$ nm, $\lambda_{em} = 324$ nm); (C) resorcinol ($\lambda_{exc} = 276$ nm, $\lambda_{em} = 304$ nm).

Table 1
Composition of the calibration and test samples

Calibration (mg L^{-1})				Test (mg L^{-1})			
Standard	Phenol	Hydroquinone	Resorcinol	Standard	Phenol	Hydroquinone	Resorcinol
C1	0.050	0.020	0.050	T1	0.080	0.024	0.080
C2	0.200	0.100	0.050	T2	0.160	0.120	0.080
C3	0.400	0.200	0.050	T3	0.320	0.180	0.080
C4	0.400	0.020	0.300	T4	0.320	0.024	0.240
C5	0.050	0.100	0.300	T5	0.080	0.120	0.240
C6	0.200	0.200	0.300	T6	0.160	0.180	0.240
C7	0.200	0.020	0.600	T7	0.160	0.024	0.400
C8	0.400	0.100	0.600	T8	0.320	0.120	0.400
C9	0.050	0.200	0.600	T9	0.080	0.180	0.400

Table 2
Optimum number of factors and statistical parameters for calibration

Analyte	Factors	REP (%)	R^2	Spectral range (nm)
Phenol	2	3.45	0.998	275–290
Hydroquinone	3	4.68	0.996	295–325
Resorcinol	2	4.20	0.996	255–305

Table 3
Analysis of real samples

Samples[a]	Phenol (mg m^{-3} air)	Hydroquinone (mg m^{-3} air)	Resorcinol (mg m^{-3} air)
1	1.30	1.50	2.29
2	1.62	1.98	3.13
3	2.04	2.90	6.56
4	1.83 ± 0.24	1.74 ± 0.26	3.47 ± 0.36

[a] Samples 1–3 are samples at different hours in the same day: 1, in the morning; 2, at midday; 3, in the afternoon; 4, mean of three replicates between days, at midday.

the extreme concentrations were 0.02–0.2 mg L^{-1} for hydroquinone, 0.05–0.6 mg L^{-1} for resorcinol and 0.05–0.4 mg L^{-1} for phenol (C1–C9 in Table 1). On the other hand, nine ternary mixtures were built with different analyte concentrations from those employed in calibration set. A full factorial design was also used, and the select concentrations for this set were into the concentration ranges of the calibration set (T1–T9 in Table 1).

3.4. Statistical parameters

The PLS model was developed in the PLS1 mode. In order to select the number of factors, the leave-one-out cross-validation method was used [21]. The criterion of Haaland and Thomas [21,22] was used for selecting the optimum number of factors. From the spectra, the appropriated wavelengths regions were selected. Table 2 shows the number of factor for each analyte, the optimal regions used in calibration, square correlation coefficient (R^2) and the relative error of prediction (REP), which give an indication of the quality of fit of all data.

3.5. Analysis of real samples

Sampling was carried out by using the technique above described, the amount of collected sample was 1.2 L of air. Table 3 shows the obtained results when the method was applied to real samples.

In order to check the traceability of the proposed method, a recovery study was carried out. From 25 mL of adsorption solution, 2 mL was taken and different concentrations of the three analytes were simultaneously added. The final volume was 10 mL. As can be seen in Table 4 the recovery percentages are successful taking into account that the sampling was done at different days.

Table 4
Study of recovery in real samples

Added (mg m^{-3} air)			Found[a] (mg m^{-3} air)			Recovery (%)		
Phenol	Hydroquinone	Resorcinol	Phenol	Hydroquinone	Resorcinol	Phenol	Hydroquinone	Resorcinol
–	–	–	1.83 ± 0.24	1.74 ± 0.26	3.47 ± 0.36	–	–	–
10.41	5.20	10.41	9.65 ± 0.90	5.38 ± 0.27	11.03 ± 0.39	92.7	103.5	105.9
20.82	12.5	41.67	20.13 ± 0.31	12.33 ± 0.79	41.67 ± 0.90	96.7	98.6	100.0

[a] $n = 3$.

4. Conclusion

The proposed method is simple and fast owing to two essential facts, one of them is the use of a fluorimeter, which is an instrument almost available in all laboratories, and it makes possible to employ this method in routine analysis. The other fact is that the sampling is very simple, the absorption solvent used to retain the analytes was water, avoiding the use of toxic organic solvents.

Moreover, it is not necessary a pre-treatment of the sample.

Additionally, the control of these phenols in the atmosphere of those rooms where smoking is allowed, is very important in the environmental caution.

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