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Detector supports: application to aliphatic amines in wastewater

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Abstract

Solid support assisted derivatization coupled to diffuse reflectance spectroscopy (DRS) was proposed and proved useful for the detection and quantification of aliphatic amines in water as an example. Dabsyl chloride (DBS), ninhydrin and sodium 1,2-naphtoquinone 4-sulphonate (NQS) were assayed as derivatization reagents. C_{18} and SDB-XC disks and C_{18} cartridges were tested for amine retention and after that derivatization. The decrease of the orange colour of dabsyl chloride on SBD-XC disks produced by the formation of its derivative with methylamine in the support (10 min at 100 °C) allowed the selective determination of the amine at concentration level equal or higher than 0.5 mg L^{-1}. Ninhydrin can be used for methylamine, ethylamine, propylamine, butylamine and pentylamine (between 5 and 15 mg L^{-1}) by measuring the diffuse reflectance produced by the brown derivative formed in C_{18} extraction disks after 15 min at 100 °C. NQS and C_{18} SPE columns can be also employed to estimate amines, but the detection limits were higher than those provided by DBS and Ninhydrin, around 10 mg L^{-1}. As an example, found concentration of methylamine or total amines (expressed as $–NH_2–N$ mg L^{-1}) in a wastewater sample is given employing dabsyl chloride or ninhydrin reagents, respectively with satisfactory results.

Keywords: Diffuse reflectance; Solid-support assisted derivatization; Amines

1. Introduction

Starting from the introduction of the assays on reagent strips [1,2], several approaches have been proposed for their extension. One of them is solid-phase extraction (SPE) when the situation dictates use of a concentration step in order to achieve the limits of detection required.

In the most used form of SPE, an aqueous sample is first treated with a reagent, the resulting complex is captured on the solid support and measured by diffuse reflectance spectroscopy (DRS) [3–5]. The use of integrating spheres (hemispherical reflectance measurement) not only achieves a simple method to extend the measure capabilities of a UV–vis spectrophotometer to reflectance measures but also improves the precision and quantitative characteristics of reflectance spectroscopy [6].

J.S. Fritz and Co. introduced colorimetric-solid-phase extraction (C-SPE). With C-SPE, a disk is directly impregnated with the colorimetric reagent. The coloured complex is therefore formed upon passage of sample solution through the disk, eliminating sample workup prior to extraction [7,8].

Since 1996, our research group has been developing a methodology in which clean up, enrichment and derivatization of the analytes are performed in a unique commercial SPE cartridge or pre-columns (in on-line systems) as a total solid-phase extraction procedure. The method is based on trapping the analyte(s) on sorbing material. The analyte is then concentrated and/or purified with a suitable solvent if necessary, and after derivatized by passing the reagent solution through the solid support. After a given reaction time the excess of the reagent is eliminated (if required) by flushing the cartridge (o pre-column) with a suitable solvent and finally, the derivatives are desorbed and collected or transferred to the analytical column in HPLC if a fully automated procedure is needed. When the extract is collected, it is measured by conventional spectrophotometry or spectrofluorimetry. Also, the

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extract can be injected in a liquid chromatograph for its separation and detection. The potential of our methodology has been illustrated for quantifying several amino-compound of interest in clinical or pharmaceutical analysis [9–15]. This methodology improves the analytical characteristics of the pre-column solution derivatization procedure. Amongst the advantages with regard to the conventional technique are: a simpler handling of samples, time savings, a better selectivity and stability of the reaction products, possibility of automation and sample enrichment. Now, our interest is focused on water analysis [16–18].

This paper extends our methodology by coupling it to reflectance diffuse spectroscopy and shows other option for developing test strips when a preconcentration step is needed for aliphatic amines in water samples. At the present time, the importance of reliable and easy-to-operate tools suitable also for on-site analysis is growing in analytical chemistry.

As is well known, aliphatic amines analysis requires a derivatization step due to they show little, if any ultraviolet (UV) or visible light absorption, fluorescence or electrochemical activity, and usually are present at very low concentrations.

A great variety of reagents have been evaluated as colorimetric derivatizing agents for compounds which contains the amino group. Between them we tested dabsyl chloride (DBS) [19,20], ninhydrin [21] and sodium 1,2-naphthoquinone-4-sulphonate (NQS) [9,11].

In this paper, we studied the couple solid-support assisted derivatization and diffuse reflectance. We also evaluated the applicability of this couple for the analysis of amines in wastewaters as an example because of the difficulty of the matrix. Utility of empore disks, C_{18} cartridges and the three reagents above mentioned were studied. The proposed assays constitute a rapid, simple and cheap way to detect and determine substances without trained personnel or complicated sample treatment.

2. Experimental section

2.1. Apparatus and reagents

A HP-8453 UV–vis spectrophotometer combined with a Labsphere RSA-HP-8453 reflectance spectroscopy accessory from Hewlett Packard (Avondale, USA) was used for all the diffuse reflectance measures. Total reflectance is composed by specular and diffuse reflection, the first one occurs in smooth surfaces and the second results by penetration of the radiation into the solid support substrate. In an attempt to determine if these phenomena affects to the quantitativety of the analysis, 8° (total reflectance) and 0° (specular excluded) reflectance measurements were done. The spectral range measured was 380–980 nm. The water samples, aqueous standards and reagents were passed through the disk by means of a solvent filtration unit. In the case of cartridges, all operations were effected by flushing the cartridges with air using a 10 mL syringe or by using the vacuum station IST VacMaster.

All the chemicals were of analytical grade and nanopure water from a Nanopure II system (Barnstead, MS, USA) was used throughout. Methylamine, ethylamine, propylamine, butylamine, pentylamine, dimethylamine and diethylamine were from Sigma (St. Louis, USA). Dabsyl chloride from Fluka (Buchs, Switzerland), ninhydrin and 1,2-naphthoquinone-4-sulfonic acid from Sigma (St. Louis, USA), were used as derivatizant reagents. Boric acid Sigma (Steinheim, Germany), sodium hydrogen carbonate from Probus (Badalona, Spain), sodium carbonate from Prolabo (Darmstadt, Germany) and sodium dihydrogen phosphate from Merck (Darmstadt, Germany) were used to prepare buffer solutions. Sodium hydroxide and hydrochloric acid from Panreac (Barcelona, Spain) were also used. Methanol was obtained from Merck (Darmstadt, Germany).

Three molar Empore high performance Extraction Disks C_{18} and SDB-XC (47 mm) and Bond Elut C_{18} 200 mg extraction columns were from Varian (Habor City, USA).

2.2. Stock standard solutions

Ninhydrin and dabsyl chloride solutions were prepared in acetone. Stock standard solutions of amines (1000 mg L^{-1}) and NQS were prepared in water. All the buffered solutions were prepared by dissolving the adequate amount of the salt or acid in water and adjusting the pH with 1 mol L^{-1} NaOH or 1 mol L^{-1} HCl.

All the derivatizing reagents were prepared daily.

Water sample employed was a water factory sample previously filtered.

2.3. Procedure

2.3.1. Procedure I. Derivatization with dabsyl chloride

C_{18} or SDB-XC extraction disks were conditioned with 5 mL of MeOH and 5 mL of water. Ten milliliter of methylamine working standard solution (0.5–2 mg L^{-1}), ethylamine, propylamine, butylamine, pentylamine, dimethylamine and diethylamine (1 mg L^{-1}) were passed through the disks. After amine retention, 1 mL of borate buffer 0.5 mol L^{-1} at pH 9 and 1 mL of dabsyl chloride 0.2×10^{-3} mol L^{-1} (prepared in acetone), previously mixed was added. The derivative formation was completed after 10 min at 100 °C in an oven. Diffuse reflectance spectrum of the disks was registered with hemipherical/8° or 0° factor.

2.3.2. Procedure II. Derivatization with ninhydrin

A quarter part of a C_{18} disk was conditioned with 0.5 mL of MeOH and 0.5 mL of water. One mililiter of working standard solution of the amine (5–25 mg L^{-1}) was dropped and passed through the disks. The amines were methylamine, ethylamine, propylamine, butylamine and pentylamine. One milliliter of acetate buffer 0.3 mol L^{-1} pH 6 mixed with 0.3 mL ninhydrin 25×10^{-3} mol L^{-1} was added to the disks.

A spot of 1.5 cm was obtained. The reflectance spectrum of the disks was registered after 15 min in the oven at 100 °C.

2.3.3. Procedure III. Derivatization with NQS

Two milliliters of working standard solutions of the amine were passed through SPE cartridges, previously conditioned with 1 mL of methanol and 1 mL of carbonate buffer 1% at pH 10.5. Concentrations of methylamine evaluated were up to 20 mg L^{-1} and for dimethylamine up to 75 mg L^{-1}. Derivatization of the retained amines was carried out by flushing the cartridges with 0.5 mL of carbonate buffer 8% at pH 10.5 followed by 0.5 mL of NQS 1.83×10^{-2} mol L^{-1}. After 15 min of reaction time the cartridges were cleaned with 2 mL of carbonate buffer 1% and 3 mL of water.

For measuring reflectance diffuse of the C_{18} sorbent, the plastic support of the SPE cartridge was broken, the adsorbent was transferred to a transparent glass plate (7.5 cm × 2.5 cm), after crashing and homogenising the coloured solid, another glass plate, with the same dimensions, was put on the first one. Finally, both plates were joined with two paperclips one in each side and then diffuse reflectance measurement was done.

2.3.4. Water sample

The water was employed diluted ten times or without dilution when the procedure with dabsyl chloride or ninhydrin, respectively was worked. Three replicates were made in each case. The water sample was also analysed by liquid chromatography using dansylation and UV–vis detection by the procedure described in [16]. The mean content found for methylamine (three replicates) was $10.1 \pm 0.5(s)$ mg L^{-1} and for pentylamine 3.8 ± 0.2 mg L^{-1}.

3. Results and discussion

3.1. Choice of the support and optimisation of the experimental conditions

3.1.1. Dabsyl chloride

Higher reflectance differences for both 0° and 8° measurements were obtained between blank and methylamine 1 mg L^{-1} with SDB-XC disks than with C_{18} disks for DBS reagent. Fig. 1 shows the % diffuse reflectance measurements at 8° for C_{18} and SDB-XC extraction disks. Worse results were obtained employing SPE cartridges. So SDB-XC extraction disks were selected as optima and used for DBS concentration study. When DBS concentration was 0.4×10^{-3} mol L^{-1} a precipitate appeared in the disks surface after heating that made the reflectance measures not suitable. 0.2×10^{-3} mol L^{-1} was the optimum concentration, 0.1×10^{-3} mol L^{-1} provided less sensitivity. Heating times and temperature were also assayed according to the literature [19,20], 10 min and 100 °C, respectively were chosen as optimum values. In an attempt to improve sensitivity, 20 mL of methylamine working standard solution was processed, but the analyte auto-eluted, so 10 mL of water sample or amine working standard solution was chosen as sample volume. The extraction efficiency of the SDB-XC disk was independent of the methylamine concentration. The obtained recoveries were 66 ± 2 (*s*, *n* = 3) and 61.2 ± 0.7(*s*, *n* = 3) for 0.5 and 2 mg L^{-1} of amine, respectively. The methylamine content was analysed in the solution spread throughout the disk by using the *o*-phthaldialdehyde-*N*-acetylcisteine (OPA-NAC) procedure described in [22].

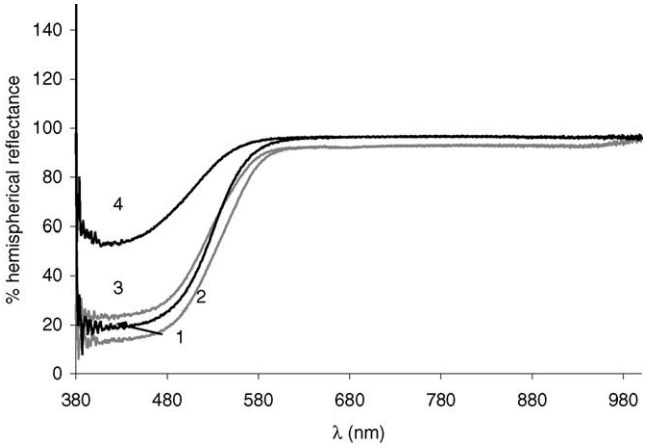

Fig. 1. Comparison between diffuse reflectance registers at 8° measures for 10 mL of a methylamine solution (1 mg L^{-1}) with dabsyl chloride as function of extraction disk sorbent: 1 and 4: blank and amine with SDB-XC extraction disks and 2 and 3: blank and amine with C_{18} extraction disks.

Orange colour of the DBS blank suffered degradation when dabsyl amine derivative was formed depending on the amine concentration. Primary amines such as methylamine, ethylamine, propylamine, butylamine and pentylamine and secondary amines such as dimethylamine and diethylamine were measured at the optimal conditions. Methylamine presented the highest signal. The other amines presented similar values to that obtained by the blank, overcoat measuring the diffuse reflectance at 8°.

3.1.2. Ninhydrin

As with dabsyl chloride, SDB-XC and C_{18} extraction disks, conditioned with 0.5 mL of MeOH and 0.5 mL of water, were studied. Fifteen minutes were chosen as heating time to form de coloured derivate because it is the most common time used in the literature [20–21]. If ninhydrin concentration was 25×10^{-3} mol L^{-1}, 5 mg L^{-1} of methylamine can be measured with C_{18} extraction disks and amine concentration must be increased until 100 mg L^{-1} with SDB disks. Besides brown colour was obtained for the derivate when C_{18} disks are employed and purple colour with SDB disks. C_{18} extraction disks were chosen because of the improved sensitivity. The extraction efficiency estimated as previously expressed for SDB-XC disk was also independent of the amine concentration. Recovery values were between 98.4 ± 0.4 (*s*, *n* = 3) and 99.76 ± 0.06 (*s*, *n* = 3). Worse results were obtained employing SPE cartridges although comparable

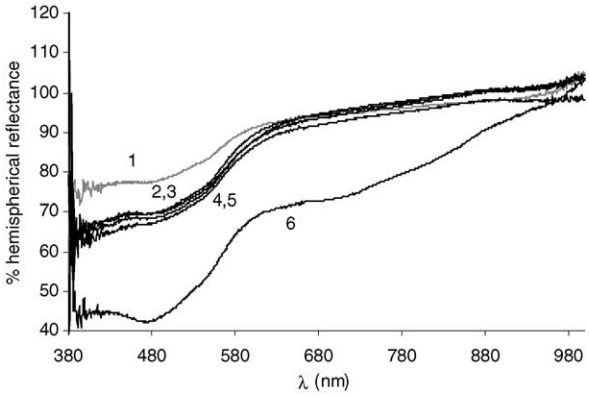

Fig. 2. Diffuse reflectance spectra at 8° obtained with ninhydrin and C_{18} extraction disks for 1: blank, 2: pentylamine, 3: propylamine, 4: butylamine, 5: ethylamine and 6: methylamine. Concentration of the amines was 10 mg L^{-1} and processed volume 1 mL.

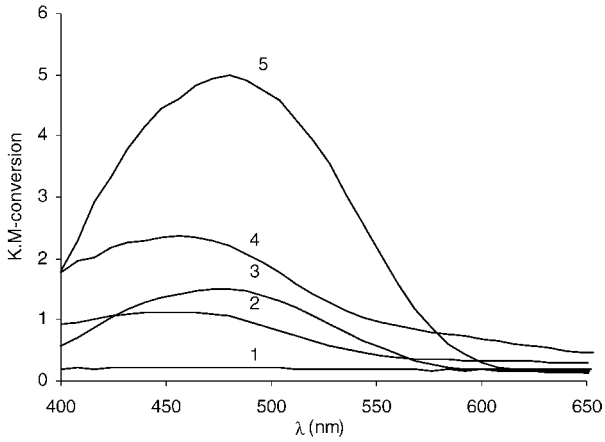

Fig. 3. Spectra obtained with Kubelka–Munk conversion for methylamine and dimethylamine standards (processed volume 2 mL) derivatized with NQS: 1: blank, 2 and 4: methylamine 10 and 20 mg L^{-1}, 3 and 5: dimethylamine 20 and 75 mg L^{-1}.

extraction efficiencies were achieved for amines. Low, medium and high concentration levels of ninhydrin were assayed. 1×10^{-3}, 25×10^{-3} and 50×10^{-3} mol L^{-1}, more colour differences and so that better sensitivity was obtained with 25×10^{-3} mol L^{-1}.

The reflectance spectra for methylamine, ethylamine, propylamine, butylamine and pentylamine (10 mg L^{-1}) are shown in Fig. 2.

3.1.3. NQS

We used previously established experimental conditions for other amines [11]. Improved results were obtained when the C_{18} adsorbent, of a commercial SPE cartridge was measured. The extraction disks provided less sensitive results. Fig. 3 shows the spectra obtained with the employed Kubelka–Munk (K–M) conversion in reflectance spectroscopy, $F(R) = (1 - R)^2/2R$, for NQS blank and several standards of methylamine and dimethylamine. The measures were done at 8° as better results were obtained in this case. Orange coloured derivates for secondary amines and dark red for primary amines were obtained.

3.2. Analytical parameters

Eight degree reflectance measures (R) were considered optima for methylamine with DBS because better calibration equations were obtained than those provided by 0° measurements (a = 33, s_a = 6, b = 40, s_b = 7, R^2 = 0.932, *Linearity* (t = 5.215, α = 0.035), n = 4, s_{yx}/b = 0.16) as the results of Table 1 show. Also these analytical signals were selective for methylamine at the concentration levels assayed. The recovery of the methylamine signal for a mixture containing methylamine (0.5 mg L^{-1}) and ethylamine, propylamine, butylamine, pentylamine, dimethylamine and diethylamine at 1 mg L^{-1} all of them, was (100.1 ± 0.7)%.

Table 1 shows the calibration equations employing both diffuse reflectance and K–M function as analytical signals at 450 nm. Better linearity was obtained employing R instead of K–M values as the t-test showed (Table 1) working with dabsyl chloride reagent. Then, the standard deviation of the procedure (s_{yx}/b) was worse for K–M values than that obtained by the use of R measurements. Consequently, better detection

Table 1
Calibration equations at 8° for amines with DBS (procedure I) for methylamine, with ninhydrin (procedure II) for methylamine, ethylamine, propylamine, butylamine and pentylamine and with NQS (procedure III) for methylamine and dimethylamine

		Direct reflectance (R) (%)						Kubelka–Munk conversion					
		$a \pm s_a$	$b \pm s_b$ (mg L^{-1})	Linearity (t, α)	R^2	n	s_{xy}/b	$a \pm s_a$	$b \pm s_b$ (mg L^{-1})	Linearity (t, α)	R^2	n	s_{xy}/b
I	MA	21 ± 1	34 ± 2	19.110, 0.000	0.992	5	0.05	1.4 ± 0.2	−1.3 ± 0.3	4.280, 0.050	0.902	5	0.19
II	MA	78 ± 3	−3.4 ± 0.5	6.771, 0.002	0.920	6	1.5	$(-8 \pm 5)10^{-2}$	$(3.7 \pm 0.8)\ 10^{-2}$	4.418, 0.012	0.830	6	2.3
	EA	86.1 ± 0.7	−1.8 ± 0.1	15.733, 0.000	0.984	6	0.6	$(7 \pm 5)10^{-3}$	$(6.3 \pm 0.8)10^{-3}$	7.591, 0.002	0.935	6	1.3
	PA	86 ± 1	−1.8 ± 0.1	12.566, 0.001	0.9845	5	0.7	$(5 \pm 7)10^{-3}$	$(6 \pm 1)10^{-3}$	6.373, 0.008	0.931	5	1.3
	BA	85.2 ± 1.1	−1.7 ± 0.2	10.890, 0.002	0.975	5	0.8	$(9 \pm 4)10^{-3}$	$(6.4 \pm 0.6)10^{-3}$	7.625, 0.005	0.972	5	0.8
	PenA	84.2 ± 1.5	−1.6 ± 0.2	7.625, 0.005	0.951	5	1.1	$(1.3 \pm 0.1)10^{-2}$	$(5.5 \pm 0.2)10^{-3}$	21.926, 0.000	0.994	5	0.4
III	MA	48 ± 5	−1.9 ± 0.8	4.949, 0.038	0.925	4	2.9	0.1 ± 0.2	0.11 ± 0.01	7.900, 0.016	0.969	4	1.8
	DMA	38 ± 8	−0.4 ± 0.1	2.686, 0.075	0.706	5	27	0.3 ± 0.1	$(5.5 \pm 0.2)10^{-2}$	19.260, 0.000	0.992	5	3.6

a: Ordinate, b: slope, s_a and s_b standard deviation of the ordinate and slope, respectively; R^2: determination coefficient, and $s_{x/y}/b$: standard deviation of the procedure.

Table 2
Found concentration of methylamine with DBS or total primary content with ninhydrin in the waste water sample

Procedure	Found methylamine mean ± S.D. (mg L^{-1})	Found N–NH2 mean ± S.D. (mg L^{-1})
HPLC-UV–vis detection	10.1 ± 0.5	–
Dabsyl detector support/reflectance	10.2 ± 0.5	–
OPA-NAC fluorescence assay	–	5.8 ± 0.3
Ninhydrin detector support/reflectance	–	6.4 ± 0.2

Comparison with the results obtained with dansylation-LC and OPA-NAC methods.

limits must be achieved by using *R* analytical signals. Bearing in mind this value the detection limit for methylamine is around 0.15 mg L^{-1}. Visually this value can be distinguished to the blank reagent. The precision (expressed as % R.S.D.) obtained for 1 mg L^{-1} of methylamine was 2 and 7% (n = 3) employing *R* and K–M signals, respectively.

By using ninhydrin reagent, the minimum concentration which made possible a qualitative analysis, by visual inspection of the brown colour derivate formed, was 5 mg L^{-1} for all amines assayed. Similar concentrations were calculated by use the approximation value to the detection limit $3s_{yx}/b$ as can be derived from Table 1 for ninhydrin. By use the standard deviation of the blank reagent (s_B) measured in three different days, the detection limits calculated as $3s_B/b$ were 3, 5, 5, 5.5 and 6 mg L^{-1} for methylamine, ethylamine, propylamine, butylamine and pentylamine, respectively. Diffuse reflectance for methylamine was also measured with 8° wedge and 0° wedge. Only 8° reflectance measures at 480 nm (Table 1) provided good linearity for methylamine compared with results at 0° (a = 81, s_a = 5, b = −2.9, s_b = 0.9, R^2 = 0.8496, *Linearity* (t = 3.362, α = 0.078), n = 4, s_{yx}/b = 2.1). The calibration curves for ethylamine, propylamine, butylamine and pentylamine at 8° are shown in Table 1. Both *R* and K–M signals provided similar quality of the calibration equations as can be seen in this table. The precision obtained for 5 mg L^{-1} of amine was between 1.7–2.3% and 8.5–15% employing *R* and K–M signals, respectively. For 10 mg L^{-1} the variation coefficients were between 2.8 and 1.4% for *R* measurements and between 6.8 and 7.5% for K–M signals.

The mean slope value for all amines obtained considering the concentration expressed as –NH_2–N mg L^{-1} and *R* measurements was 7.9 mg L^{-1} with a standard deviation of 1.5. The mean ordinate value was 83.9 and the standard deviation 3.3. These values could be used to estimate total amine groups.

The analytical parameters for methyl- and dimethylamine with direct reflectance signals and Kubelka–Munk function at 480 and 460 nm with NQS derivatizing agent, respectively are given in Table 1. The linearity of the calibration graph, when the Kubelka–Munk conversion was employed was better than that obtained with direct reflectance measurements. The linear interval for methylamine was up to 20 mg L^{-1} and for dimethylamine up to 75 mg L^{-1}. The detection limits achieved by use of NQS reagent, around 10 mg L^{-1} were worse than those obtained with the previous studied reagents, dabsyl chloride and ninhydrin. The precision obtained was 10% for K–M signals.

3.3. Utility

The procedure with dabsyl chloride was used to estimate selectively methylamine in the wastewater, containing also pentylamine as LC method provided (see experimental section). Table 2 shows the found concentration obtained with the dabsyl solid support and diffuse reflectance measurement. It was in accordance with the methylamine content determined with dansylation and LC. This unbiased procedure achieves selectivity for methylamine determination without using a chromatographic technique. It could be used as a screening procedure of samples in order to reduce costs and saving time in the environmental laboratory or for in situ determinations. It is important when a high number of samples must be processed. In our knowledge, a method with such characteristics does not exist in the literature.

Total primary amine content was estimated by using ninhydrin procedure. The obtained value expressed as –NH_2–N mg L^{-1} (see Table 2), is consistent with the composition found by liquid chromatography and similar to the value given in paper [22] for the same water but analysed by fluorimetry using *o*-phthaldialdehyde-*N*-acetylcisteine reagent (Table 2). This procedure is an alternative method to the fluorimetric OPA-NAC method proposed in [22].

4. Conclusions

This paper shows the possibility of coupling the solid-support assisted derivatization proposed by our research group by first time in 1996 and the diffuse reflectance spectroscopy technique. The analysis of amines in water samples was chosen as an example.

Utility of empore disks, C_{18} cartridges and three reagents, dabsyl chloride, ninhydrin and NQS were studied. In all cases, the coupling is possible by choosing the best support and the derivatization conditions. The calibration step was studied for the three reagents. Increase and decrease signals with the increase of amine concentration were tested. *R* measurements and K–M transformation were evaluated.

The reagent conditioned the detection limits and the linear interval of concentrations. DBS provided the best detection limits and mainly was selective for methylamine. This detector support permits to work without liquid chromatography for this derivatization reagent and for methylamine determination. Ninhydrin can be employed to determine total primary amine groups. NQS provided worse detection limits but it

could be improved by processing higher volumes of water than those used in the present work avoiding liquid–liquid extraction necessary to separate NQS-derivatives.

The proposed assays constitute a rapid, simple and cheap way to detect and determine substances without trained personnel or complicated sample treatment. Also, the assays kept stable at less six months and then, the detector supports could be filed during this period of time.

The outlined characteristics make the procedures especially suitable for screening of samples and control or monitoring analysis in environmental laboratories or for in situ determinations.

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References

[1] B. Walter, Anal. Chem. 55 (1983) 499A.
[2] A. Zipp, W.E. Hornby, Talanta 31 (1984) 863.
[3] S.G. Dmitrienko, O.A. Sviridova, L.N. Pyatkova, V.A. Zhukova, Y.A. Zolotov, Anal. Chim. Acta 405 (2000) 231.
[4] S.G. Dmitrienko, O.M. Medvedeva, A.A. Ivanov, O.A. Shipigun, Y.A. Zolotov, Anal. Chim. Acta 469 (2002) 295.
[5] M. Miró, W. Frenzel, J.M. Estela, V. Cerdá, Analyst 126 (2001) 1740.
[6] A. Gauch, J. Rima, A. Charef, J. Suptil, C. Fachinger, M. Martin-Bouyer, Talanta 48 (1999) 385.
[7] M.P. Arena, M.D. Porter, J.S. Fritz, Anal. Chem. 74 (2002) 185.
[8] M.P. Arena, M.D. Porter, J.S. Fritz, Anal. Chim. Acta 482 (2003) 197.
[9] P. Campíns-Falcó, A. Sevillano-Cabeza, C. Molins-Legua, M. Kohlman, J. Chromagr. 687 (1996) 239.
[10] R. Herráez-Hernández, P. Campíns-Falcó, A. Sevillano-Cabeza, Anal. Chem. 68 (1996) 734.
[11] P. Campíns-Falcó, C. Molins-Legua, A. Sevillano-Cabeza, R. Porras-Serrano, Analyst 122 (1997) 673.
[12] R. Herráez-Hernández, P. Campíns-Falcó, A. Sevillano-Cabeza, I. Trümpler, Anal. Chim. Acta 334 (1997) 125.
[13] C. Molins-Legua, P. Campíns-Falcó, A. Sevillano-Cabeza, Anal. Chim. Acta 378 (1999) 83.
[14] C. Molins-Legua, P. Campíns-Falcó, A. Sevillano-Cabeza, M. Pedrón-Pons, Analyst 124 (1999) 477.
[15] C. Molins-Legua, P. Campíns-Falcó, S. Meseguer Lloret, Chromatographia 58 (2003) 1.
[16] J. Verdú-Andrés, P. Campíns-Falcó, R. Herráez-Hernández, Analyst 126 (2001) 1683.
[17] S. Meseguer-Lloret, C. Molins-Legua, P. Campíns-Falcó, J. Chromatogr. A. 978 (2002) 59.
[18] J. Verdú-Andrés, P. Campíns-Falcó, R. Herráez-Hernández, Chromatographia 55 (2002) 129.
[19] L. Perbellini, L. Maestri, N. Veronese, S. Romani, F. Brugnone, J. Chromatogr. B. 759 (2001) 349.
[20] M.A. Castillo, R.C. Castells, J. Chromatogr. A. 921 (2001) 121.
[21] G. Fang, N. Liu, Anal. Chim. Acta 445 (2001) 245.
[22] A. Sevillano Cabeza, Y. Moliner Martinez, C. Molins-Legua, P. Campíns-Falcó, Anal. Bioanal. Chem. 376 (2003) 918.