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Determination of 5-dodecylsalicylaldoxime and 5-nonylsalicylaldoxime in commercial extractants by high-performance liquid chromatography with photometric detection

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Abstract

A liquid chromatographic method with photometric detection was developed and validated for the determination of 5-dodecylsalicylaldoxime in the industrial extractants LIX 622 and LIX 860 and 5-nonylsalicylaldoxime in LIX 622N, Acorga PT5050 and Acorga P5100. The limit of detection was 2.18 μg/ml for 5-dodecylsalicylaldoxime and 2.06 μg/ml for 5-nonylsalicylaldoxime. Good linear relations between the areas and the concentration of the standard injected were found in the range of 5–100 μg/ml and reproducibility studies yielded relative standard deviations lower than 6.12% in all the cases.
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1. Introduction

Industrial extractants based on 5-dodecylsalicylaldoxime (LIX 860, LIX 622) or 5-nonylsalicylaldoxime (LIX 622N, Acorga PT5050, Acorga P5100) are used to recover heavy metals, mainly copper, from acidic media [1–3]. They contain, apart from the active components, industrial solvents of high molecular mass and modifiers such as tridecanol (LIX 622, LIX 622N, Acorga PT5050) or nonylphenol (Acorga P5100). No information on their exact composition is available.

In order to study, from the thermodynamic point of view, the chemical reactions taking place between the metal ion and the active component of the extractant in liquid–liquid extraction processes, it is necessary to know accurately the temperature, ionic strength, pH and metal and ligand concentrations. All variables can be easily fixed except the ligand concentration when industrial extractants of unknown composition are used.

In this sense, some indirect methods, such as the last loading of copper [4] are used to determine the concentration of the active component. This method consists of equilibrating organic solutions of extractants with an aqueous phase containing a high concentration (0.5 M) of copper at pH 4 at which the extractant is known to be fully loaded with copper. Copper is then stripped to an aqueous solution at low pH and concentration of ligand is calculated assuming the formation of species CuL_2, where HL denotes the molecule of hydroxyoxime.

Up till now, few works regarding the use of HPLC for α-hydroxyoxime extractants or alkylsalicylaldoxime derivatives have been published. Sowa et al. [5] proposed a method for the identification of the *anti* and *syn* isomers of hydroxyoxime in LIX 65N and for the components of LIX 71. Concerning the detection of 5-nonylsalicylaldoxime, 4-nonylphenol and 5-nonylsalicylaldehyde several columns, mobile phases and detection wavelengths were reported by Stone et al. [6]. The degradation products of hydroxyoxime containing extractants (LIX 984N, M5640) have been analysed by Cheng et al. [7]. A gradient elution with acetonitrile (62–95%)–KH_2PO_4 (0.5 mM, pH 2.6) was performed. In any case, very wide peaks were obtained.

On the other hand, studying the therapeutical applications of salicylaldoxime derivatives, a method for the quantification of salicylaldoxime and β-resorcylaldoxime has been reported [8]. These compounds are similar to alkylsalicylaldoximes but they do not contain the alkylic chain. Nikupaavo et al. [9] have proposed a method for quantify-

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ing 5-dodecylsalicylaldoxime and 3-chloro-5-dodecylsalicylaldoxime, with no application to real samples.

The aim of this work was the development of an HPLC method for the quantification of 5-dodecylsalicylaldoxime and 5-nonylsalicylaldoxime in some commercially available extractants. For this purpose, the works of Nikupaavo et al. [9] and Stone et al. [6] have been compared with our studies.

2. Experimental

2.1. Reagents and solutions

The reagents LIX 860-IC (90% (w/w) of 5-dodecylsalicylaldoxime and 10% (w/w) of ShellSolD70) and LIX 860N-IC (90% (w/w) of 5-nonylsalicylaldoxime and 10% (w/w) of ShellSolD70), used as standards and the commercial extractants LIX 860, LIX 622 and LIX 622N were kindly supplied by Cognis Ireland (Little Island, Co., Cork, Ireland). Samples of Acorga PT5050 and Acorga P5100 were kindly supplied by Avecia (Phoenix, AZ, USA).

Tetrahydrofuran was purchased from Romil super purity solvent. Water from Milli-RO and Milli-Q systems (Waters) was used.

Stock solutions containing 1000 μg/ml of the above mentioned standards were prepared in tetrahydrofuran (THF). Calibration standards (5–100 μg/ml) were prepared by weighing the appropriate volumes of the stock solutions in THF–water (50:50 (v/v)).

2.2. Instrumentation

The ultraviolet spectra were recorded with a Shimadzu 260 (Kyoto, Japan) double beam spectrophotometer. The 5 ml quartz cuvettes were used. Wavelength was varied between 210 and 400 nm.

The HPLC system consisted of a four channels Waters (Milford, MA, USA) 600 pump, equipped with a 20 μl injection loop. The pump operated through a Waters 600 controller. The chromatographic separations were performed on a NovaPak C_{18} column, 150 mm × 3.9 mm i.d., 5 μm particle size, Waters (Barcelona, Spain). Photometric detection was performed using a Waters 2487 dual-wavelength UV-absorbance detector. The detection wavelength was set at 314 and 285 nm.

The chromatographic data were collected with the software Millennium Chromatography Manager purchased from Waters.

2.3. Chromatographic conditions

Mobile phases were previously filtered through a 0.45 μm pore diameter polyvinyliden difluoride membrane (Millipore HVLP) and degassed by bubbling helium throughout. The separation of analytes was performed at room temperature, at a flow rate of 1.0 ml/min.

3. Results

3.1. Optimisation of the chromatographic system

Previous to the optimisation of the chromatographic system it was necessary to check the absorption spectra of the compounds at several mobile phases The same spectra was obtained in all the cases. Fig. 1 compares the UV-Vis spectra of the standard ligands (5-dodecylsalicylaldoxime and 5-nonylsalicylaldoxime) with that of the extractants, Acorga PT5050 and Acorga P5100 under one of the studied conditions. It can be appreciated that the spectra of both 5-alkylsalicylaldoxime are superimposed. Acorga PT5050 also gives the same spectrum, whereas that of Acorga P5100 shows an additional band at 285 nm. This band can be due to the absorption of 4-nonylphenol, in agreement with the results of Stone et al. [6]. The spectra of the other extractants (LIX 860, LIX 622 and LIX 622N) were similar to that of the standards.

Three bands were obtained at 220, 262 and 314 nm. The first band at 220 nm was rejected due to the low selectivity of shorter wavelengths, since many compounds absorb at this region. The band at 262 nm was also rejected because 4-nonylphenol, an impurity present in some samples as a subproduct of the process of manufacture, as a degradation product or even as a modifier (Acorga P5100), would interfere (λ_{max}: 285 nm). In spite of the lower sensitivity of the band at 314 nm, we selected it as working wavelength due to its higher selectivity.

The selectivity of the proposed wavelength should be corroborated in the chromatographic system. In order to achieve the greater separations between the oximes and the phenols a THF–water (55:45 (v/v)) mobile phase was selected. The low elution force of this mobile phase, and thus

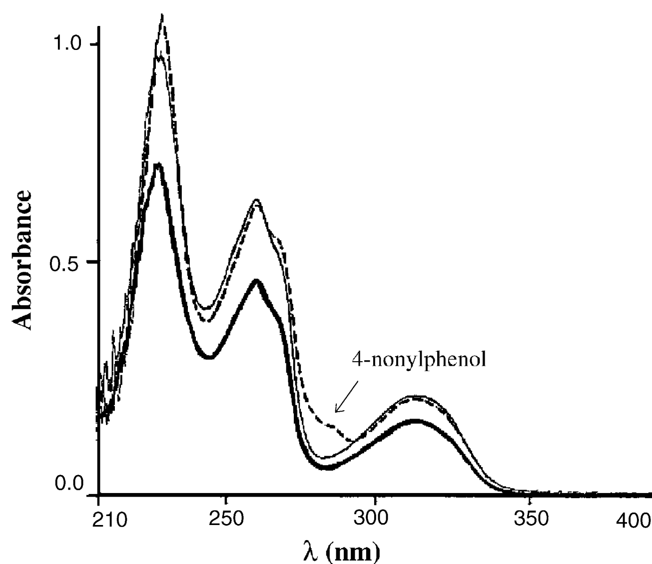

Fig. 1. UV-Vis spectra of: 5-dodecylsalicylaldoxime and 5-nonylsalicylaldoxime (▬); Acorga PT5050 (—); and Acorga P5100 (- - -) dissolved in THF–water (70:30 (v/v)).

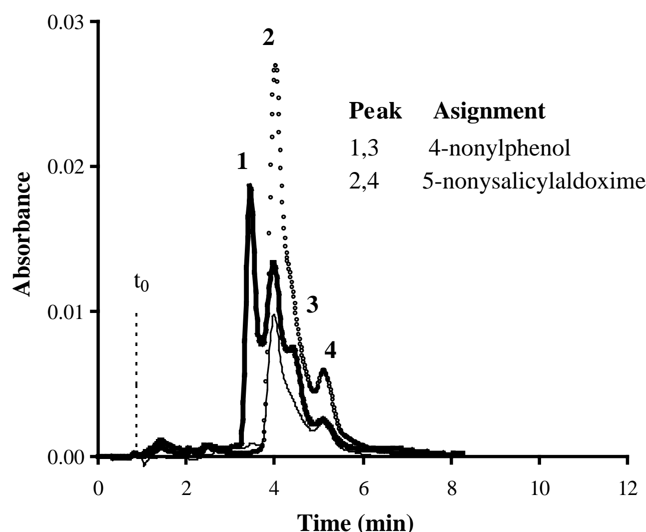

Fig. 2. Chromatograms of 50 μg/ml samples of: the commercial extractants Acorga P5100, λ = 285 nm (▬); Acorga P5100 λ = 314 nm (···); and Acorga PT5050, λ = 285 nm (—); THF–water (55:45 (v/v)); flow rate = 1 ml/min; t_0 = 0.85 min.

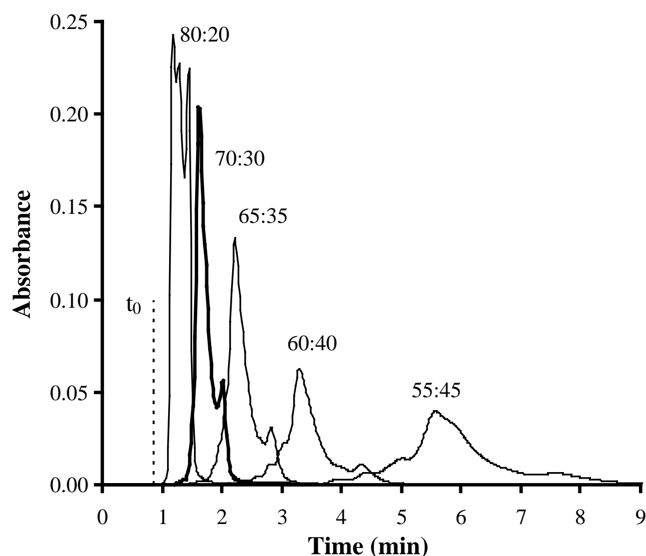

Fig. 3. Chromatograms of 200 μg/ml samples of the commercial extractant LIX 622 varying THF–water proportion in the mobile phase, λ = 314 nm; flow rate = 1 ml/min; t_0 = 0.85 min.

the high retention times obtained, allowed the separation of the analytes and the additives of the sample. First, the chromatograms of Acorga PT5050 and Acorga P5100 at a wavelength of 285 nm were obtained and compared (Fig. 2). The chromatogram of Acorga P5100 (5-nonylsalicylaldoxime and 4-nonylphenol) is composed of four badly resolved peaks at retention times of approximately 3.47, 4.00, 4.43 and 5.17 min, whereas the chromatogram of Acorga PT5050 (5-nonylsalicylaldoxime and tridecanol) shows only two peaks at 4.00 and 5.17 min. Thus, the first and third peaks (3.47 and 4.43 min) of Acorga P5100 can be attributed to nonylphenols, whereas the rest of the peaks (4.00 and 5.17 min) correspond to 5-nonylsalicylaldoxime isomers.

Acorga P5100 was injected in the chromatographic system at a wavelength of 314 nm (Fig. 2). In this case, the chromatogram obtained was identical in shape to that of Acorga PT5050 at 285 nm, thus corroborating the high selectivity of the detection at 314 nm for alkylsalicylaldoximes.

The same procedure was applied to the chromatographic characterisation of industrial extractants based on 5-dodecylsalicylaldoxime, obtaining similar results.

The next step was the optimisation of the percentage of organic modifier for an optimum quantification of the analytes. Since the presence of interfering peaks in the chromatogram could be avoided by means of the utilisation of an adequate wavelength, the proportion of THF in the mobile phase was increased. Fig. 3 shows the results obtained at several mobile phase compositions. It can be appreciated that the composition of the mobile phase THF–water (70:30 (v/v)) gives rise to more symmetric peaks and also decreases the analysis time.

Finally, Fig. 4 shows the chromatograms of standards and samples under the selected conditions (λ = 314 nm, THF–H_2O, 70:30 (v/v)). It can be appreciated that the samples LIX 860 and LIX 622 elute between 1.52 and 2.27 min, with two maxima at 1.73 and 2.05 min, as the standard LIX 860-IC. The samples LIX 622N, Acorga PT5050 and Acorga P5100, as well as the standard LIX 860N-IC elute at a shorter time, between 1.50 and 2.05 min, with two maxima approximately at 1.58 and 1.87 min. In both cases, the analytes are well separated from the observed injection peak (t_0: 0.85 min).

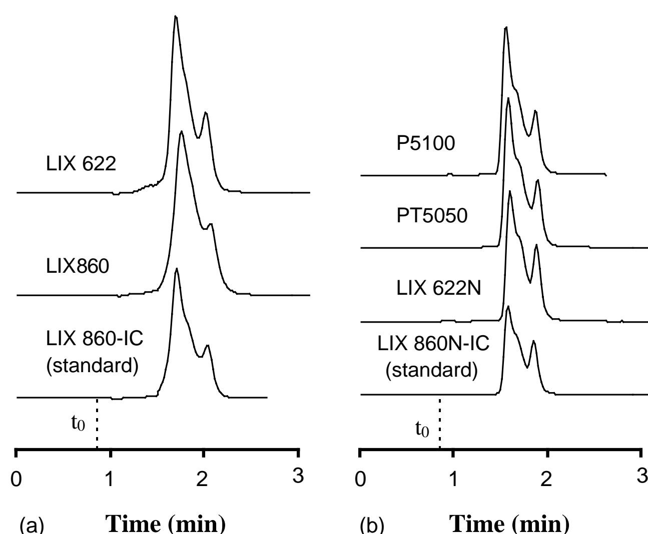

Fig. 4. Chromatograms of 50 μg/ml solutions of the standards and 100 μg/ml samples of the commercial extractants, λ = 314 nm; THF–water (70:30 (v/v)); flow rate = 1 ml/min; t_0 = 0.85 min. Analytes: (a) 5-dodecylsalicylaldoxime; (b) 5-nonylsalicylaldoxime.

Table 1
Statistical parameters of the calibration of 5-dodecylsalicylaldoxime and 5-nonylsalicylaldoxime. $\lambda = 314$ nm

	Analyte	
	5-Dodecylsalicylaldoxime	5-Nonylsalicylaldoxime
Retention range (min)	1.52–2.27	1.50–2.05
Linear range (μg/ml)	5–100	5–100
Slope ± σ	$(15.23 \pm 0.16) \times 10^3$	$(19.13 \pm 0.28) \times 10^3$
Intercept ± σ	$(2.34 \pm 7.82) \times 10^3$	$(25.96 \pm 14.20) \times 10^3$
r^2	0.9997	0.9994
Intra-day repeatability R.S.D. (%) (5/50/100 μg/ml)[a]	1.45/1.92/2.98	3.05/2.64/1.62
Inter-day repeatability R.S.D. (%) (5/50/100 μg/ml)[a]	6.12/4.28/3.60	0.58/3.19/2.64
Detection limit (μg/ml)	2.18	2.06
Quantification limit (μg/ml)	7.62	10.04

THF–water (70:30 (v/v)). Flow rate = 1 ml/min.
[a] $n = 3$.

3.2. HPLC method validation

The calibration curves for 5-dodecylsalicylaldoxime and 5-nonylsalicylaldoxime were linear in the concentration range from 5 to 100 μg/ml. The peak area–concentration relationships were linear until at least 1500 μg/ml (the solubility in the mixture THF–water, 50:50).

The linear regression equation obtained for 5-dodecylsalicylaldoxime was $y = (15.23\pm0.16)\times10^3x+(2.34\pm7.82)\times10^3$ ($r^2 = 0.9997$), whereas that for 5-nonylsalicylaldoxime was $y = (19.13\pm0.28)\times10^3x+(25.96\pm14.20)\times10^3$ ($r^2 = 0.9994$), where y and x are the peak area and concentration (μg/ml) of the standards, respectively.

The reproducibility of the chromatographic method for both compounds was tested at 5, 50 and 100 μg/ml, injecting each standard three times for 3 consecutive days.

The data collected were treated using the analysis of variance (ANOVA) method [10]. The R.S.D. (%) was always below 6.12%, thus showing the high stability of the system.

Limits of detection (LODs) and quantitation (LOQs) have been calculated as 3 and 10 times the total deviation of the calibration curves, respectively. Values for LOD of 2.18 μg/ml and LOQ of 7.62 μg/ml were obtained for 5-dodecylsalicylaldoxime, whereas LOD of 2.06 μg/ml and LOQ of 10.04 μg/ml were obtained for 5-nonylsalicylaldoxime.

The quantitative and statistic parameters calculated for both systems are collected in Table 1.

3.3. Analytical applications

The method was applied for the determination of 5-dodecylsalicylaldoxime in the commercial extractants LIX 622 and LIX 860, and 5-nonylsalicylaldoxime in the commercial products LIX 622N, Acorga PT5050 and Acorga P5100, all made into THF–H_2O, 50:50 (v:v), to yield a concentration of about 100 μg/ml of the total sample. Three different aliquots of each extractant were prepared and immediately injected in the chromatographic system. The mean value was collected. The obtained mass percentage of 5-alkylsalicylaldoxime in the commercial extractants is shown in Table 2.

Table 2
Composition of some industrial extractants

Extractant	Active component	Percentage (w/w) $\pm (t/\sqrt{Np})\sigma$
LIX 860	5-Dodecylsalicylaldoxime	64.82 ± 0.96
LIX 622	5-Dodecylsalicylaldoxime	67.70 ± 0.52
LIX 622 N	5-Nonylsalicylaldoxime	55.3 ± 1.7
Acorga PT5050	5-Nonylsalicylaldoxime	56.71 ± 0.72
Acorga P 5100	5-Nonylsalicylaldoxime	53.1 ± 2.8

N_p = number of aliquots = 3; σ = standard deviation of the samples; t = Student parameter for a 95% confidence level.

4. Discussion

The proposed method has been successfully applied to the quantification of 5-dodecylsalicylaldoxime in LIX 860 and LIX 622 and 5-nonylsalicylaldoxime in LIX 622N, Acorga PT5050 and Acorga P5100. It is the first time that a complete chromatographic method has been developed and applied for this purpose.

The resolution of this technique is not enough to allow the separation of all the isomeric forms that compose the products. Other more powerful techniques, such as gas chromatography [11,12] allow better separation of the isomers although the multiple peaks obtained made difficult the quantification of the total amount of hydroxyoximes.

Although resolution between several isomers is not an important factor the same cannot be said regarding alkylsalicylaldoximes and alkylphenols. In our case, this problem has been solved by the use of wavelength at 314 nm, which is more selective than those previously used in the determination of similar compounds [6,9].

Regarding the repeatability of the method, similar results than those of Nikupaavo et al. [9] were obtained although their method was more sensitive. However, sensitivity is

not a problem for samples such as industrial extractants in which the active component concentration is usually high.

The selectivity achieved by using the appropriate wavelength allows the coelution of analyte and interferents. Mobile phases with high percentage of organic modifiers can be used and fast and simple determination of the analytes is achieved.

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