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Talanta 43 (1996) 1117–1124

Talanta

Polarographic study of acrolein and its determination by flow injection with amperometric detection at a mercury electrode

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Received 11 August 1995; revised 3 January 1996; accepted 11 January 1996

Abstract

A study of the electrochemical behavior of acrolein at a dropping mercury electrode using different polarographic techniques is described. Theoretical studies of the reversibility of the wave of acrolein were carried out using two different polarographic techniques: direct current tast and differential pulse. Differential pulse polarography may be used to determine acrolein concentration in a Britton–Robinson buffer solution of pH 10 in the ranges 2×10^{-7}–10^{-8} and 5×10^{-8}–10^{-4} mol dm^{-3} and a coefficient of variation of 1.7% for a concentration of 10^{-5} mol dm^{-3}. A flow injection method with amperometric detection at a potential of -1.4 V using a mercury electrode is also described. Before each injection, any drop hanging from the tip of the capillary needs to be dislodged and a new electrode drop dispensed; three different drop sizes were tested. A linear relationship between peak intensity and acrolein concentration was obtained in the range 10^{-5}–10^{-7} mol dm^{-3}, with a detection limit of 9.8×10^{-8} mol dm^{-} 3 and a coefficient of variation of 2.9% for a 2×10^{-7} mol dm^{-3} concentration. Several organic and inorganic species were tested in order to ascertain whether they interfered with the signal for acrolein. The proposed methods were applied to the determination of acrolein in seawater samples.

Keywords: Acrolein determination; Flow injection; Polarography

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1. Introduction

Acrolein (2-propenal) is considered a prioritary pollutant according to the US Environmental Protection Agency [1,2]. Acrolein can be found in the gas phase of cigarette smoke and environmental tobacco smoke [3], in exhaust emission from heavy-duty diesel vehicles and diesel engines [4] and in different aqueous media [5–7].

Several methods to determine acrolein after derivatization have been developed; these methods are based on the formation of formaldehyde and colorimetric detection with chromotropic acid [6], and derivatization with 2,4-dinitrophenylhidrazine and its determination by HPLC with ultraviolet or diode-array detection [8,9]. Gas chromatography has been applied to the determination of acrolein [10,11], usually in combination

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PII S0039-9140(96)01873-5

with mass spectrometry [3,12].

A wide variety of electroanalytical techniques have been reported, such as d.c. [13,14], oscillopolarographic [15] and differential pulse methods at a mercury or glassy carbon electrode [5,16], with detection limits of about 10^{-6} mol dm^{-3}. Polarography finds use in all fields of chemical analysis. Among various polarographic methods, differential pulse polarography is most useful in environmental chemistry, chiefly because of its high sensitivity, good selectivity and wide application range. Amperometric detection is the simplest and by far the most common measuring technique for flow measurements. Amperometry can be a very reliable detection approach, and good detection limits are often feasible.

In this work, different polarographic techniques were used to study the reduction of acrolein at a dropping mercury electrode, reaching very low concentration levels for its determination. Moreover, a flow injection method with amperometric detection at a mercury electrode has been developed.

2. Experimental

2.1. Apparatus

A Metrohm 646 Va processor equipped with a model 647 VA stand was used for polarographic studies. A dropping mercury electrode, an Ag/AgCl/3 M KCl reference electrode and a platinum auxiliary electrode were installed in the stand. An inert gas was used to operate the mercury electrode. The maximum inert gas pressure required was 1 ± 0.2 bar. The mercury electrode was equipped with a glass capillary with an internal diameter of 0.05 mm and an Hg flow rate of 1.37 mg s^{-1} (0.1 mm^3 s^{-1}) was obtained. In the differential pulse technique, during the voltage ramp a voltage pulse was applied during the last 40 ms of the drop life. The pulse amplitude can be preselected. The current was measured by integration for 20 ms immediately before the start of the pulse, and again for 20 ms towards the end of the pulse.

The flow injection system consisted of a Gilson Minipuls-2 peristaltic pump and a Rheodyne 5020 sample injection valve with variable injection volumes. The electrochemical cell was a Princeton Applied Research Model 420 mercury LC electrode equipped with a flow cell, an Ag/AgCl reference electrode and a platinum counter electrode. Three mercury drop sizes were available: small, medium and large. The drop sizes were in a volume ratio series of 1:2:4, corresponding to an area ratio series of 1:1.6:2.5. The electrochemical cell was connected to a Princeton Applied Research Model 400 electrochemical detector. During the experiments, the detector was operated in the d.c. mode. The injection system was connected to the flow cell through 0.5 mm i.d. PTFE tubing. A Hewlett-Packard Model 862/D X–Y recorder was coupled to the electrochemical detector. All measurements were carried out at room temperature.

2.2. Reagents and solutions

Aqueous acrolein (Merck, analytical reagent grade) stock solutions (10^{-1} mol dm^{-3}) were prepared in doubly distilled water; appropriate dilutions were made daily from a freshly prepared stock solution by dilution with doubly distilled water.

A Britton–Robinson buffer solution containing 2.7 g of boric acid, 2.3 ml of acetic acid and 2.7 ml of orthophosphoric acid (85%) per litre was used as electrolyte and carrier solution. Different pH values were adjusted by using 1 M NaOH solution.

Nitrogen was used as the inert gas to purge the analyte solutions and to operate the mercury electrode. Calibraiton graphs were carried out with two different inert gas pressures.

2.3. Procedures

2.3.1. Polographic studies

A 50 ml volume of Britton–Robinson buffer solution at pH 10 was placed in the electrochemical cell. After purging with nitrogen, 50 μl of acrolein solution were added to the buffer solution and the polarogram was recorded with a

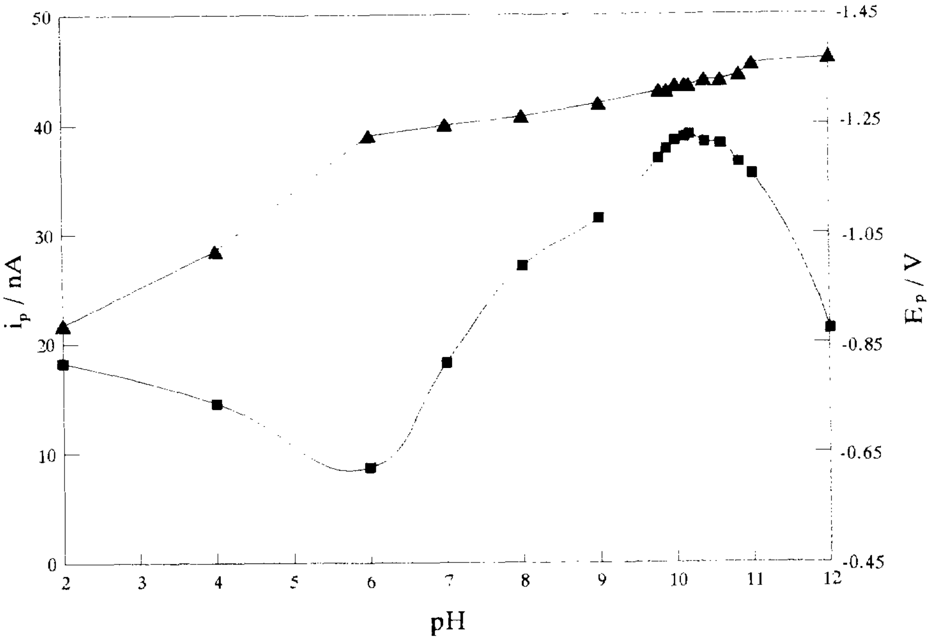

Fig. 1. Effect of pH on (▲) E_p and (■) i_p for 10^{-5} mol dm^{-3} acrolein concentration. Pulse amplitude, -50 mV; scan rate, 10 mV s^{-1}; drop time, 0.4 s.

drop time of 1 s, a scan rate of 4 mV s^{-1} and a potential range from -1.1 to -1.5 V. Theoretical studies of the reversibility of the wave of acrolein were carried out using two different polarographic techniques: d.c. tast and differential pulse.

2.3.2. Determination of acrolein in spiked seawater

For the determination by differential pulse polarography, 25 ml of spiked seawater and 7 ml of 0.25 mol dm^{-3} EDTA are transferred into a 50 ml calibrated flask and filled with Britton–Robinson buffer solution of pH 10. The analytical solution is introduced into the electrochemical cell. After purging with nitrogen, a pulse amplitude of -100 mV is applied, with a scan rate of 4 mV s^{-1} and a drop time of 1 s. The acrolein concentration is calculated by the standard additions method.

When the flow system is used, 250 μl of a solution containing 25 ml of spiked seawater and 7 ml of 0.25 mol dm^{-3} EDTA are injected into the carrier solution (flow rate 1.8 ml min^{-1}), and the detection is performed at a potential of -1.4 V. Before each injection, any drop hanging from the tip of the capillary needs to be dislodged and a new electrode drop manually dispensed.

3. Results and discussion

3.1. Determination of acrolein by differential pulse polarography

The peak potential, E_p, showed a dependence on pH in the range studied, 2.0–12.0. More negative E_p values were obtained with increasing pH. The peak current, i_p, vs. pH showed a complex shape. First, i_p decreased slightly with increasing pH in the range 2–6. A strong increase in i_p was observed in the pH range 6–10, after which another decrease was obtained. Well defined reduction peaks were obtained in basic media, and i_p reached its maximum value at pH 10; this pH value was chosen for further studies. Fig. 1 shows the influence of pH on i_p and E_p.

The influence of different buffer solutions is shown in Table 1. The solutions were prepared at pH 10 and different ionic strengths. A slight in-

Table 1
Influence of different buffer solutions

Buffer solution	Ionic strength	i_p(nA)	E_p(V)
Britton-Robinson	0.2	43.2	−1.31
	0.1	39.4	−1.32
	0.05	37.9	−1.33
Sodium hydrogen carbonate–sodium carbonate	0.2	43.3	−1.32
	0.1	41.3	−1.33
	0.05	38.8	−1.34
Boric acid–potassium chloride–sodium hydroxide	0.1	39.8	−1.32
	0.05	38.1	−1.33

crement in i_p was observed on increasing the ionic strength. The use of buffer solutions other than Britton–Robinson leads to no significant differences in i_p. The peak potential remains virtually constant with increasing ionic strength and when different buffer solutions are used.

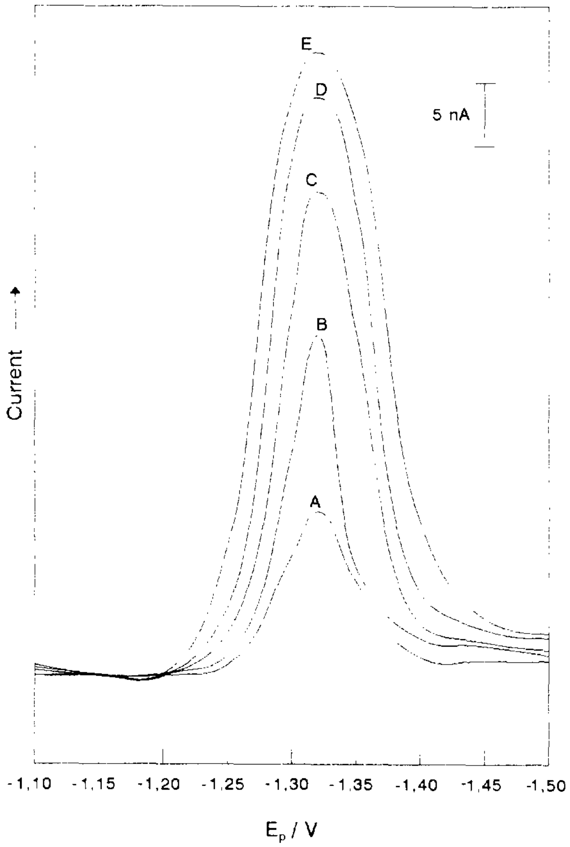

Fig. 2. Voltammograms for different pulse amplitudes for a concentration of 10^{-5} mol dm^{-3}: A, −25; B, −50; C, −75; D, −100; and E, −125 mV. Scan rate, 10 mV s^{-1}; drop time, 0.4 s.

The improvement in selectivity and the measuring sensitivity attained depend on a proper choice of the pulse attidue, ΔE: from the point of view of the selectivity, ΔE should be as small as possible, whereas the measuring sensitivity increases, up to a certain value, with increasing ΔE. The effect of this parameter was studied over the range −25 to −125 mV. The peak height increased with increase in pulse amplitude; the relationship between i_p and ΔE was linear in the range −25 to −100 mV. The peak width and the residual current also increased with increasing ΔE. A value of −100 mV was chosen as a compromise between sensitivity and selectivity. Voltammograms for different values of ΔE are shown in Fig. 2.

The influence of drop time was studied in the range 0.1–1.2 s. For drop times longer than 1 s no increase in i_p was observed; this value was used for subsequent studies in order to improve the sensitivity.

The calibration graphs were found to be linear in the concentration ranges 10^{-8}–2×10^{-7} mol dm^{-3} ($r = 0.9999$, nitrogen pressure 1 bar) and 5×10^{-8}–10^{-4} mol dm^{-3} ($r = 0.9999$, nitrogen pressure 0.7 bar) with slopes of 19.97 and 16.76 mA dm^{-3} mol^{-1}, respectively. The detection limit was 2.5×10^{-9} mol dm^{-3} and the coefficient of variation at a concentraiton of 10^{-5} mol dm^{-3} was 1.7% ($n = 16$).

The influence of several organic and inorganic species on the acrolein signal was tested. All the organic compounds had at least one carbonyl group; some of them were unsaturated com-

Table 2
Effect of interferent species on the determination of acrolein by differential pulse polarography (DPP) and by flow injection with amperometric detection (FIA)

Interferent	Interferent to acrolein ratio	Deviation (%) DPP	FIA
Acetaldehyde	200:1	−0.1	−24.6
Formaldehyde	200:1	+0.9	−56.6
2-Hydroxybenzaldehyde	10:1	−7.9	−9.6
2-Nitrobenzaldehyde	1:1	+16.1	−8.6
Isophthalaldehyde	1:1	–[a]	+1.8
Phenyl 2-pyridyl ketone	10:1	−22.1	+49.7
2,3-Butanedione	200:1	−23.9	>100
1,2-Cyclohexanedione	200:1	−17.2	−12.6
5,5-Dimethyl-1,3-cyclohexanedione	200:1	+0.3	−1.5
Acetophenone	200:1	−2.9	+1.6
Ni^{2+}	200:1	−2.9	>100
Co^{2+}	200:1	−5.7	>100
Cu^{2+}	200:1	+1.2	>100
Pb^{2+}	200:1	+4.7	−1.0
Mg^{2+}	200:1	+3.3	>100
No_3^-	200:1	+0.4	+0.5
SO_4^{2-}	200:1	+10.8	−2.3
Co_3^{2-}	200:1	+10.4	−1.2

[a] No signal for acrolein was observed.

pounds. For 10^{-5} mol dm^{-3} of acrolein, solutions containing different interferent to acrolein ratios in the range 200:1 to 1:1 were tested. The results obtained (Table 2) show that acrolein can be determined in the presence of acetaldehyde, formaldehyde, dimedone and acetophenone at the maximum concentration ratio, and in the presence of salicylaldehyde at a 10:1 ratio, with deviations below 8%. None of the inorganic species tested were found to interfere at a 200:1 ratio.

Recovery studies were carried out on different seawater samples spiked with acrolein. The analytical solutions contained 5×10^{-6}, 1.5×10^{-6}, 5×10^{-7} or 10^{-7} mol dm^{-3} of acrolein. Recoveries in the range 91–102% were obtained; for the lower concentrations, recoveries of about 98% were reached.

3.2. *Electrochemical reversibility*

A study of the reversibility of the wave of acrolein was carried out using two different techniques: d.c. tast and differential pulse polarography. A 10^{-5} mol dm^{-3} acrolein solution buffered with Britton–Robinson solution of pH 10 was employed.

3.3. *D.c. polarography*

The reversibility of the process was investigated by means of logarithmic analysis of the polarograms. The electrode potential was plotted versus $\log|(i_L - i)/i|$, corresponding to most irreversible and simple reversible reductions [17]. For two different samples, a linear relationship (with $r = 0.990$ and 0.997) was observed, with slope values of 0.035 and 0.035, the half-wave potential, $E_{1/2}$, being −1.303 and −1.309 V. From these values, and considering the expression of the slope ($b = 0.059/\alpha n$), the approximate numbers of electrons exchanged (n) were 1.66 and 1.65. Similar results were obtained by application of Tome's criterion ($E_{1/2} - E_{3/4} = 0.059/n$), with $n = 1.84$ and 1.62.

3.4. *Differential pulse polarography*

For a reversible process, the following expressions are reported:

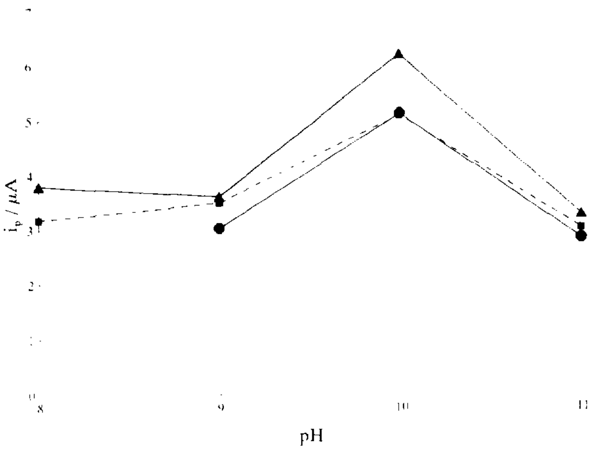

Fig. 3. Influence of pH on i_p when a large drop size is used for a detection potential of (▲) −1.4, (■) −1.5 and (●) −1.6 mV. Acrolein concentration, 10^{-4} mol dm^{-3}; injection volume, 0.25 ml; flow rate, 1.8 ml min^{-1}.

$i_p^a/i_p^c = 1$; $E_p^c - E_p^a = |\Delta E|$

The experimental values are 0.23 and 38 mV ($|\Delta E| = -100$ mV), respectively. According to Birke et al. [18], this indicates, for $\alpha \geqslant 0.5$, a quasi-reversible charge transfer. On the other hand, according to Rodriguez-Monge et al. [19], the inequality $i_p^c > i_p^a$ indicates either an irreversible process (E_i) or an electrode process followed by a chemical step (EC), the distinction between them being given by the value of $W_{1/2}$ for waves obtained with values of $\alpha n \Delta E$ in the range 0–20 mV, since then $\alpha n W_{1/2} = 90$ mV. An almost integral value of n indicates an EC process, whereas a decimal value would characterize an E_i process. The experimental results, for $\Delta E = -5$ mV, gave $W_{1/2} = 59.7$ mV and $\alpha n = 1.5$.

According to the electrochemical study carried out, acrolein is reduced via an irreversible electrode process. The waves correspond to the reduction of the carbonyl group by two electrons and two protons to an alcohol group.

3.5. *Determination of acrolein by FIA*

Various experiments were carried out during the optimization studies. The influence of drop size was studied at three detection potentials (−1.4, −1.5 and −1.6 V) and in the pH range 8–11. Three mercury drop sizes were available: small, medium and large. The drop sizes were in a volume ratio series 1:2:4, corresponding to an area ratio series of 1:1.6:2.5.

The influence of pH on peak height at the three different detection potentials is shown in Fig. 3. When the large drop size is used, the best response is obtained at a potential of −1.4 V over the whole pH range. In any case, the intensity of pH 10 is always greater than that for other pH values. Fig. 4 shows the influence of pH on intensity at a potential of −1.4 V for the different drop sizes. As expected, the peak height increases when a large drop size is used. These conditions were maintained in subsequent studies.

The peak height and peak width in flow systems depend on the dispersion of the sample during its passage from the injector to the detector. The flow rate and injection volume were selected as a compromise between sensitivity and sampling capacity. Fig. 5 shows the effect of flow rate and injection volume on i_p. The peak width and the residence time decreased with increasing flow rate, whereas they increased with increasing injection volume. An increase in the signal was observed as the flow rate increased from 0.25 to 1.8 ml min^{-1}; a value of 1.8 ml min^{-1} was chosen to improve the sensitivity (peak height). Similar variations were found for injection volumes in the range 0.1–1 ml. When an injection volume of 1 ml is used, a higher peak height is reached and a sampling frequency of 57 h^{-1} is obtained. In order to obtain good sensitivity without an excessive de-

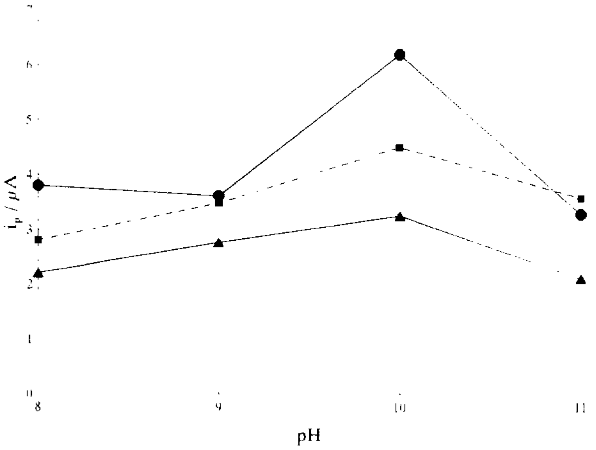

Fig. 4. Influence of pH on i_p for the three different drop sizes: (●) large, (■) medium and (▲) small. Detection potential −1.4 mV; acrolein concentration, 10^{-4} mol dm^{-3}; injection volume, 0.25 ml; flow rate, 1.8 ml min^{-1}.

crease in sampling capacity, a sample loop of 0.25 ml was chosen. Under these conditions, the residence time was 20 s and the extrapolated peak width 25 s. The sample volume was diluted by a factor of three as estimated from the extrapolated peak width expressed in volume units (0.75 ml); the system would then be considered as a limited dispersion system [20]. The current reached its baseline value about 35 s after an injection, allowing a sampling frequency of about 100 h^{-1}. The tube length between the injection valve and the detector can be kept as short as possible (30 cm) because no chemical reaction is involved.

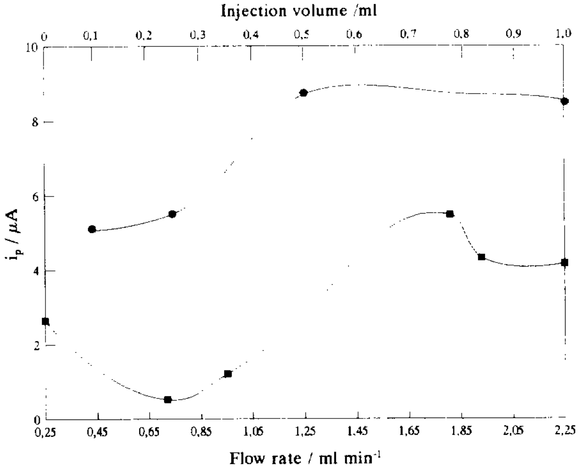

Fig. 5. Effects of (●) injection volume and (■) flow rate on i_p for a concentration of 10^{-4} mol dm^{-3}. Detection potential, −1.4 V.

The influence of acrolein concentration on i_p was investigated; a linear relationship was found in the concentration ranges 10^{-7}–10^{-6} mol dm^{-3} ($r = 0.998$) and 10^{-6}–10^{-5} mol dm^{-3} ($r = 0.991$), with slopes of 408 and 88 mA dm^{-3} mol^{-1}, respectively. The detection limit was 9.8×10^{-8} mol dm^{-3} and the coefficient of variation at a concentration of 2×10^{-7} mol dm^{-3} was 2.9% ($n = 11$).

Several species were tested by flow injection in order to ascertain whether they interfered with the signals for acrolein. The same interferent to acrolein ratios as in the differential pulse polarographic studies were used. The results are shown in Table 2.

Interference from other electroactive species was observed. At a 200:1 ratio, Co^{2+}, Cu^{2+} and Ni^{2+} were found to interfere with deviation up to 100%.

Two organic compounds showed no interference (deviations below 10%) at an interferent to acrolein ratio of 200:1 (dimedone and acetophenone) and some others showed no interference at different ratios (2-nitrobenzaldehyde and isophthalaldehyde, 1:1; salicylaldehyde, 10:1). The selectivity with direct determination is less than that obtained by the polarographic method, but it can be improved for complex samples when electrochemical detection following liquid chromatography is used.

The proposed method has been applied to the direct determination of acrolein in spiked seawater. The injected solutions contained 4.5×10^{-7}, 4.5×10^{-6} or 8.9×10^{-6} mol dm^{-3} of acrolein. Recoveries in the range 96–105% were obtained. Recoveries of about 96% were obtained when the 4.5×10^{-7} solution was injected. The determination was carried out by the standard additions method.

Acknowledgements

The authors are grateful to the CICYT (Project AMB 92-0863) for financial support.

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