

A. LIBERATORI*, S. CAPRI*, T. LA NOCE*, L. LORETI*

DETERMINATION OF ISOCYANATES IN WATER SAMPLES BY IR SPECTROPHOTOMETRY

An accurate and precise method of determining isocyanates and evaluating their stability in water is proposed. This method is based on the measurement of the absorbance at 2255 cm^{-1} wavenumber. The ability of this measurement to be assumed as assessment of "total isocyanates" is also evaluated.

1. INTRODUCTION

In recent years, an interest in determining isocyanates in environmental samples has been growing. Isocyanates are toxic and mucosal irritants, and problems of lungs can result from inhaling them. These pollutants have been found in workplace atmosphere during the production of polyurethane foams, elastomers, coatings and adhesives [1]. Isocyanates can be also found in soil as products of herbicide degradation. Finally, the presence of isocyanides in water cannot be excluded because their hydrolysis is not rapid [2] and seems to happen only in alkaline solutions [3]. In any case, acute toxicity effects can actually be foreseen.

In many countries, to limit exposure the threshold limit values in air have been set for several isocyanates. The US Department of Health, Education and Welfare has set criteria for recommended standards for occupational exposure to diisocyanates [4] and the UK Health and Safety Commission has set a "common control limit" for workplace exposure to "all isocyanates" [5]. Because of their dangerous properties, isocyanates have been included in the list of toxic and dangerous

* Istituto di Ricerca sulle Acque, C.N.R., via Reno n° 1 - 00198 Roma, Italy.

substances annexed to the EEC Council Directive of March 1978 (78/319 EEC). In 1982, these rules came into force in Italy as a result of presidential decree no. 915.

There are several techniques for the determination of isocyanates (spectrophotometry, high performance thin layer chromatography, high performance liquid chromatography, gas chromatography, etc.), but most of the proposed methods have not been found able to determine "total isocyanates", as required in many legislations and sets of regulations [1], [4], [5], [6]. In fact, chromatographic methods can be used to control dangerous known pollutants, but unknown compounds can escape detection. On the other hand, colorimetric methods, based on the reduction of aromatic isocyanates to the corresponding amines and their diazotization and coupling, are characterized by the following disadvantages: these methods do not offer very high sensitivity, linear isocyanates cannot be determined and aromatic amines can interfere.

In this work, the ability of the infrared spectrophotometric technique to determine isocyanates has been studied. Tests have been performed with a large spectrum of isocyanates to evaluate the ability of the 2255 cm^{-1} absorbance measurement to be assumed as "total isocyanates" sumparameter.

The applications of this technique in determining isocyanates in different matrices have been also evaluated. Procedures for sampling isocyanates from air are reported in the above mentioned literature. In this work, tests in aqueous solution have been also performed with the aim to evaluate both the hydrolysis rate of different compounds and the accuracy and precision of the whole procedure.

2. EXPERIMENTAL

2.1. APPARATUS

Infrared spectrophotometer, Perkin-Elmer, Mod. 283, with NaCl cells of 5 mm pathlength was applied.

2.2. REAGENTS

The reagents used (carbon tetrachloride, anhydrous sodium sulfate, sodium chloride, toluendiisocyanate, propylisocyanate, isopropylisocyanate, 3-methoxyphenylisocyanate, 4-methoxyphenylisocyanate, phenylisocyanate) were of analytical grade.

2.3. STANDARD SOLUTIONS

Standard solutions of isocyanates were prepared either in carbon tetrachloride or in water by rapid weighing and dissolving known amounts of standard.

2.4. EXTRACTION

An adequate volume of aqueous solutions was placed in a separatory funnel, and 5 g of sodium chloride were added. It was then extracted with 3 subsequent 15 cm³ portions of CCl₄. The organic phase was collected after 1 min, dried on anhydrous sodium sulfate, filtered into a 50 cm³ calibrated flask and adjusted to volume.

2.5. DETERMINATION

CCl₄ solutions were read against a CCl₄ blank test at 2255 cm⁻¹ wavenumber using a IR spectrophotometer, Perkin Elmer, Mod. 283, with NaCl cells of 5 mm pathlength (scan rate 3800 cm⁻¹/300 min, response 8, slit program 5).

3. RESULTS AND DISCUSSION

3.1. LINEARITY

Calibration graphs were constructed by plotting the absorbance values of CCl₄ solutions of every isocyanate vs their concentration expressed as $-N=C=O$ (fig. 1). In all the cases a good linear relationship was obtained.

3.2. EFFECT OF SUBSTITUENTS

The effects of substituents on absorption wavenumber and absorptivity of isocyanate have been evaluated. Table 1 shows the results obtained from equimolar solutions of various isocyanates. The absorption wavenumber varies slightly for differently substituted isocyanates: the greatest difference among the wavenumbers obtained from measurements of the tested isocyanates does not exceed 10 units (it corresponds at most to 2 mm). Absorptivity ranges from 1.65 to 3.60 mg⁻¹ cm, and differences from 4-methoxyphenylisocyanate taken as reference compound do not exceed 50%. These seem acceptable values for "sumparameter".

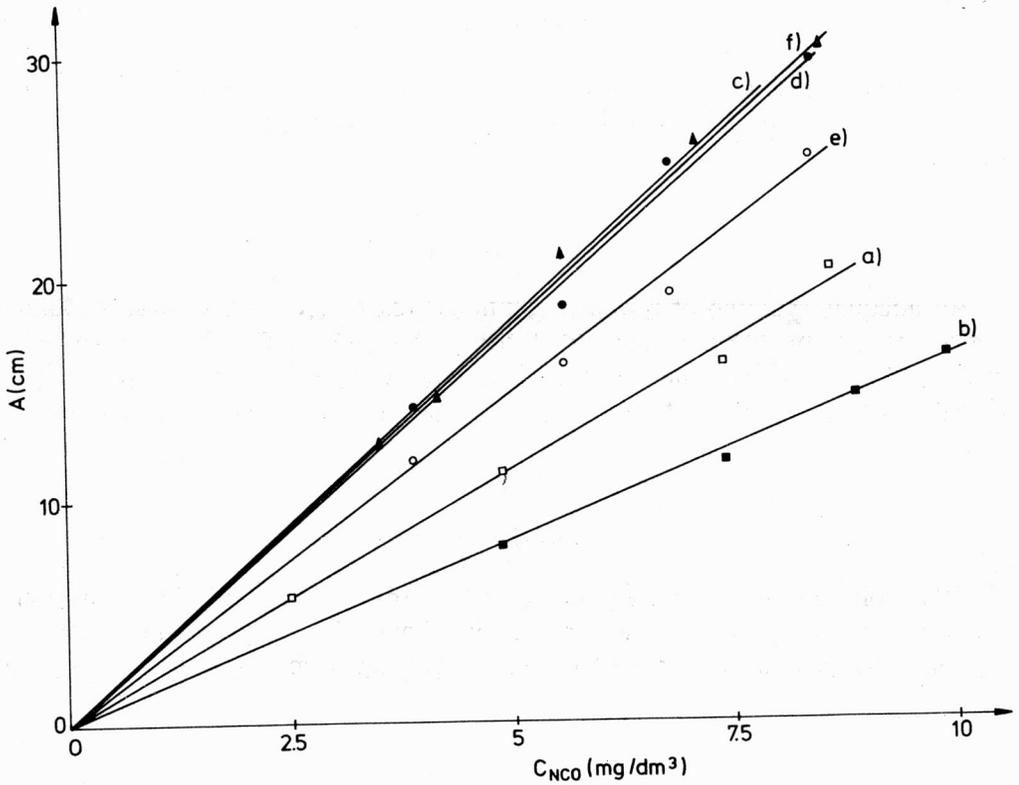


Fig. 1. Calibration graphs of differently substituted isocyanates
 a) isopropyl-, b) propyl-, c) phenyl-, d) 3-methoxyphenyl-, e) 4-methoxyphenyl-, f) toluendiisocyanate

Table 1
 Effect of substituents on wavenumber and absorptivity

| Compound | Wavenumber (cm^{-1}) | Absorptivity (mg^{-1}/cm) |
|---------------------------|------------------------------------|--|
| Propylisocyanate | 2248 | 1.65 |
| Isopropylisocyanate | 2250 | 2.29 |
| Phenylisocyanate | 2249 | 3.60 |
| 3-Methoxyphenylisocyanate | 2255 | 3.55 |
| 4-Methoxyphenylisocyanate | 2264 | 2.95 |
| Toluendiisocyanate | 2260 | 3.59 |

3.3. PRECISION AND ACCURACY

The repeatability of this technique was evaluated as relative standard deviation from the calibration plot obtained by the least square method. The results

are reported in tab. 2 and indicate that the relative standard deviations are acceptable and show very little variation.

Recovery tests and precision tests were performed on water samples at a prefixed concentration of isocyanate. The results are shown in tab. 3. They indicate recoveries ranging from 95 to 107%, and relative standard deviations ranging from 1.2 to 5.6.

Table 2

| Repeatability tests | | |
|---------------------------|-----------------------------|--|
| Compound | Relative standard deviation | Range of concentration (mg/dm ³) |
| Propylisocyanate | 1.6 | 4.9-9.9 |
| Isopropylisocyanate | 14.5 | 2.5-8.6 |
| Phenylisocyanate | 14.9 | 3.5-8.5 |
| 3-Methoxyphenylisocyanate | 18.0 | 3.8-8.6 |
| 4-Methoxyphenylisocyanate | 4.6 | 3.9-8.4 |
| Toluendiisocyanate | 0.4 | 5.9-24.0 |

Table 3

| Accuracy and precision tests | | | | |
|------------------------------|-----------------------|------------------|--------------|-------------------------------------|
| Compound | Absorbance calculated | Absorbance found | Recovery (%) | Relative standard deviation (n = 4) |
| Toluendiisocyanate | 54 | 51.2 | 95 | 4.9 |
| 4-Methoxyphenylisocyanate | 47 | 50.5 | 107 | 1.2 |
| Propylisocyanate | 53 | 53 | 100 | 1.5 |
| Isopropylisocyanate | 50 | 48 | 96 | 5.6 |
| Phenylisocyanate | 44 | 42.5 | 97 | 2.6 |
| 3-Methoxyphenylisocyanate | 57 | 59.2 | 104 | 1.6 |

3.4. STABILITY IN AQUEOUS SOLUTION

The stability of isocyanates in aqueous solution was evaluated by measuring their concentration in function of time. Figure 2 shows that their decrease follows a common way, except for toluendiisocyanate whose concentration is about constant. In this case problems for the environment can really exist because of the very slow degradation rate of isocyanates. In all the other cases the concentrations decreased to 10-35% after two days.

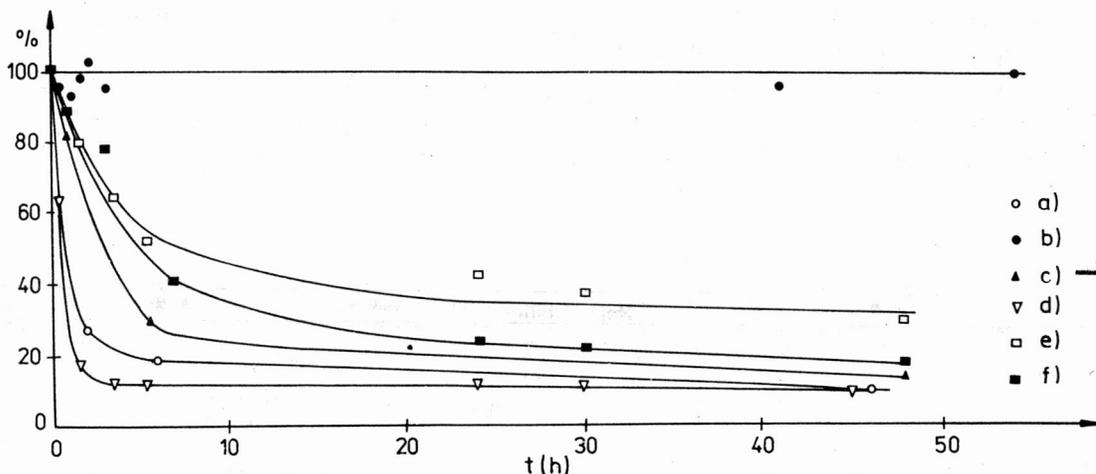


Fig. 2. Stability of isocyanates in aqueous solution

a) isopropyl-, b) toluendiiso-, c) 4-methoxyphenyl, d) propyl-, e) phenyl-, f) 3-methoxyphenyl-

4. CONCLUSIONS

The infrared method has been proved to be suitable for the determination of isocyanates and precision and accuracy tests gave acceptable values. The infrared measurement of the absorbance at 2255 cm^{-1} might be assumed as "sumparameter". In fact, absorption wavenumbers of very differently substituted isocyanates vary very slightly ($2248\text{--}2264\text{ cm}^{-1}$), and the relevant absorptivities do not exceed 50% compared with the 4-methoxyphenylisocyanate taken as reference compound. The method is rapid, selective and sensitive. The results obtained suggest its utilization in environmental samples.

Tests involving other, differently substituted isocyanates are in progress, and the results seem to agree with these conclusions.

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OZNACZANIE IZOOCYJANIANÓW W WODZIE METODĄ SPEKTROFOTOMETRII IR

Zaproponowano dokładną metodę oznaczania izocyjaninów i określania ich stabilności w wodzie. Metoda polega na pomiarze absorbancji dla liczby falowej wynoszącej 2255 cm^{-1} . Przedstawiona metoda pozwala również na oznaczenie całkowitej zawartości izocyjanianów w próbach wody.

ОПРЕДЕЛЕНИЕ ИЗОЦИАНАТОВ В ВОДЕ СПЕКТРОМЕТРИЧЕСКИМ МЕТОДОМ IR

Предложен новый метод определения изоцианатов и определения их стабильности в воде. Метод заключается в измерении поглощения для волнового числа, составляющего 2255 см^{-1} . Представленный метод позволяет также определить полное содержание изоцианатов в пробах воды.