SOME APPLICATIONS OF INFRARED AND ULTRAVIOLET SPECTROSCOPY FOR THE TOXICOLOGICAL EXAMINATION OF MEDICAL PLASTIC PRODUCTS

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Summary

IR and UV spectroscopy were used to determine the concentrations of di(2-ethylhexyl)phthalate, acrylonitrile and styrene in some medical plastic products. Both methods, based on the Lambert–Beer law, are simple, rapid and accurate. Moreover, the advantage of IR spectroscopical method is a check on what kind of plasticizer was used in the plastic because the plasticizer applied for medical purposes should have medical clearance. The measured results obtained by the two methods are presented in the paper.

The toxicity of the components in plastics for medical uses (monomers, stabilizers, dyes, plasticizers, etc.) has been a serious problem [1] which remains even nowadays a comprehensive field for research workers, biologists and toxicologists [2]. As the medical plastic products for single use are in most cases in direct contact with the human organism it is important and necessary to control and monitor the amount of the additives, admixtures and ingredients leached from plastics and to evaluate the biological ~~and~~ toxicological activities of those dissolved.

This paper is concerned with the determination of di(2-ethylhexyl)phthalate (abbr. DEHP) leached from plasticized poly(vinyl chloride) (PVC) by IR spectroscopy, and with the measurement of acrylonitrile and styrene in styrene-acrylonitrile (SAN) copolymers and in acrylonitrile-butadiene-styrene (ABS) terpolymers by UV spectroscopy.

Some medical devices made of plasticized PVC are bags for blood transfusion, for infusion, catheters and infant-care necessities. SAN and ABS are widely used for example as dialysis apparatus parts, incubator covers.

Gas chromatography has been used very often for the determination of phthalate-plasticizers [3], of styrene [4] and of acrylonitrile [7].

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Wancheck et al. employed liquid chromatography [5] to measure the amount of free styrene in plastic.

UV spectroscopy is a very suitable method for the quantitative determination of styrene [6] but we find no paper in the literature for UV spectroscopical determination of acrylonitrile.

This may be explained by the absorption maximum of acrylonitrile being at low wavelength (*208 nm*), and the spectroscopists do not work readily in this region because of the interference of the apparatus and solution.

Experimental

IR spectroscopy

A SPECORD 75 IR spectrophotometer, employing 0.612 mm sealed liquid cells, and spectroscopic grade tetrachloromethane as solvent were used. The spectra were recorded between 4000 and 400 cm^{-1}. The accuracy of the weighing of DEHP was 0.1 mg.

UV spectroscopy

A SPECORD UV VIS spectrophotometer with 1 cm quartz cells was used. To extract and dissolve acrylonitrile and styrene, aqueous ethanol (96%) is the ideal solvent. The accuracy of the weighing was 0.1 mg. The spectra were recorded between 200 and 270 nm.

Results and discussion

IR spectroscopic method

For medical plastic products made of plasticized PVC only a medical grade plasticizer having medical clearance can be used. The most accepted one of them is di(2-ethylhexyl)phthalate (DEHP) [2].

IR spectroscopy was applied in two ways: on the one hand examining carefully the spectrum of the leached plasticizer we can check that indeed a medically cleared plasticizer was used in the product, on the other hand the amount of the identified additive leached with distilled water or physiological salt solution, then extracted with tetrachloromethane, can be quantitatively measured.

Figure 1 shows the IR spectrum of di(2-ethylhexyl)phthalate.

Identification of this phthalate-ester follows from the shapes and th relative intensities of the bands, compared with each other, absorbing in th range of "carbon-hydrogen stretching vibrations". The bands are assigne with the system of assignation proposed by "Sohár–Holly–Varsányi".

For the quantitative determination of di(2-ethylhexyl)phthalate the mos suitable band is the intensive "ester carbonyl" band appearing at 1730 cm^{-1} To compensate the relative insensibility of IR spectroscopy for quantitativ measurement, the phthalate-ester was extracted with tetrachloromethane an was concentrated by evaporation to a small volume.

Table 1 gives the calculated absorbances of carbonyl band as a function o concentration of DEHP.

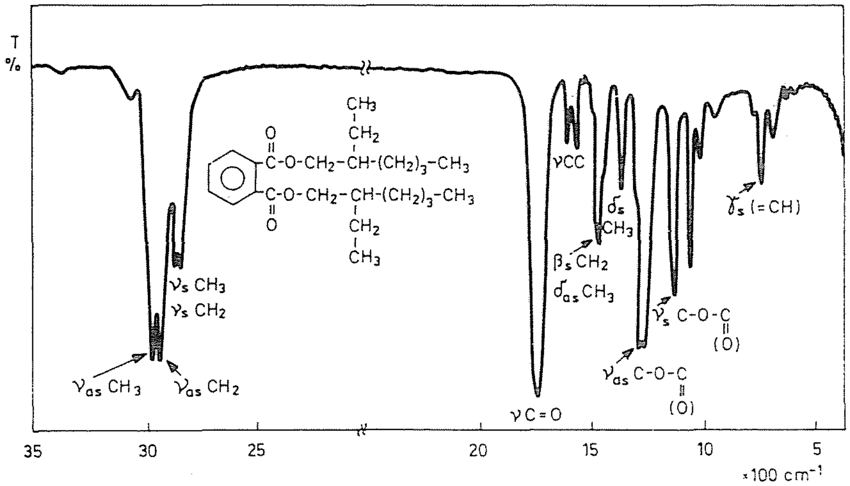

Fig. 1. IR spectrum of di(2-ethyl-hexyl)phthalate

Table 1

Measured data for the quantitative IR spectroscopical determination of di(2-ethylhexyl) phthalate

DEHP Concn g/100 cm^3	A_{1730}	$A^{1\%}_{0.612}(1730)$
0.1	0.164	1.64
0.2	0.324	1.62
0.3	0.483	1.61
0.4	0.636	1.59
0.5	0.809	1.62

Table 2

Leaching of plasticizer measured from products made of plasticized PVC

Product	The amount of DEHP leached with dist. water, mg/100 cm^3	Limit value $\frac{mg}{100\,cm^3}$
Bag for peritoneal dialysis	<0.1	1.0
Vein catheter	0.5	1.0
Feeding tube	1.4	2.0
Laryngeal cannula	0.2	2.0
Recumbent surface of incubator	1.7	5.0
Baby napkin	<0.1	5.0

The calculated specific absorbances (absorptivities) show that the calibration curve proves a linear relationship.

Some measured results relating to the leached amount of plasticizer (DEHP) from products made of plasticized PVC manufactured in Hungary are presented in Table 2. IR spectroscopic method was used to determine the amount of DEHP to be leached out by distilled water.

UV spectroscopic method

Some important medical products are made of SAN and ABS, respectively (SAN: styrene-acrylonitrile copolymer, ABS: acrylonitrile-butadiene-styrene terpolymer). Some of them are e.g.: capillardialyzator chamber, incubator cover, tongue-depressor etc. With these products, the danger of toxic monomers being present and the possible chance of leaching are to be reckoned with. Acrylonitrile is a strong respiratory-organic poison that can be absorbed through the skin, too. This is why styrene and acrylonitrile should be controlled in medical plastic products. Styrene is also a dangerous monomer.

UV spectroscopy is a very useful tool in the determination of styrene, because it is a "UV-chromophore" substance, consequently its extract with aqueous ethanolic solution can be quite simply measured.

Figure 2 shows the UV spectra of styrene and acrylonitrile.

Both maxima of styrene are suitable for quantitative determination. The detection limit of the method is 0.5–1.0 mg/dm^3. Figure 3 depicts the calibration of the determination of styrene and acrylonitrile in aqueous ethanolic solution.

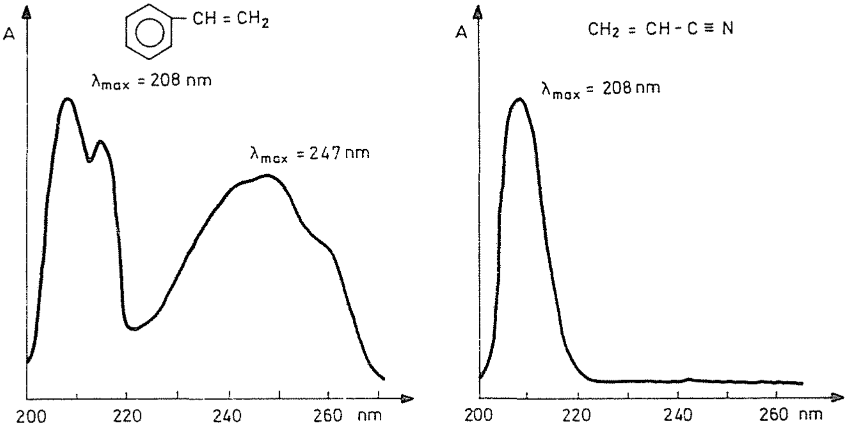

Fig. 2. UV spectra of styrene and asoylonitule

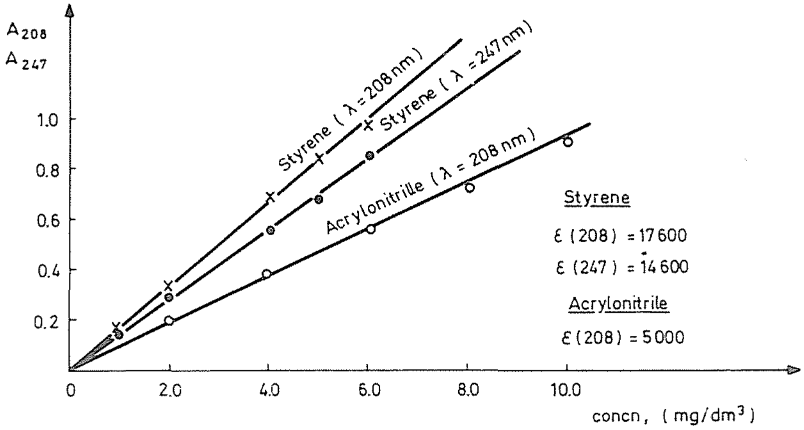

Fig. 3. Calibration straights for the determination of styrene and acrylonitrile

Acrylonitrile has also UV absorption, but due to its structure only one transition appears at 208 nm (see Fig. 2). In spite of the fact that the absorption band of acrylonitrile can be found low in the wavelength range, we have proved that the band can be said not to be a "Phoney maximum" because with the calibrational series made of pure acrylonitrile, the concentration vs. absorbance relationship shows linear correlation (see Fig. 3).

The fact that the absorption maxima of acrylonitrile and styrene at 208 nm overlap makes difficult the simultaneous measurement of the two monomers extracted from SAN and ABS. However, at a given wavelength the absorbances measured are simply added therefore being taken into con-

Table 3

The measured monomer content of some products

Product	Raw material	Concn of styrene µg/g	Concn of acrylonitrile µg/g
Tongue-depressor for single use	Polystyrene	130	–
Incubator cover	SAN	132	8
Capillardialyzator house	SAN	72	68
Air channel of incubator	ABS	448	0
Limit value	Polystyrene SAN ABS	500	10

sideration the intensity ratio of two absorptional bands of styrene, it can be calculated what the additive member at 208 nm is.

The latter corresponds to the absorption represented by acrylonitrile, which characterizes unambiguously its concentration. The detection limit of the method is 1.0 mg/dm^3.

Table 3 lists the measured monomer contents of some products examined by this method.

The determination of both monomers is very simple, reproducible and easy to carry out.

References

1. LEFAUX, R.: Chimie et Toxicologie des Matiéres Plastiques, Compagnie Française d'Editions, Paris, 1964
2. KEVY, S. V.–JACOBSON, M. S.: Environmental Health Perspectives *45*, 57 (1982)
3. HAASE, H.: Kautschuk Gummi Kunststoffe *20*, 501 (1967)
4. STEICHEN, R. J.: Anal. Chem. *48*, 1398 (1976)
5. WANCHECK, P. L.–WOLFRAM, L. E.: Appl. Spectrosc. *30*, 542 (1976)
6. KENNEDY, T.–TAUBINGER, R. P.: Analyst *94*, 625 (1969)
7. JEFFS, A. R.: Analyst *94*, 249 (1969)

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