Journal of Photochemistry, 36 (1987) 211 - 219

PHOTOLYSIS STUDY OF THE SUSPENSION BENZALDEHYDE SOLUTION–SILICA GEL[†]

M. ČEPPAN[a], L. LAPČÍK[a], M. VESELÝ[a] and M. ŠIVOVÁ[b]

[a] *Department of Textile, Pulp and Paper, Slovak Technical University, 812 37 Bratislava (Czechoslovakia)*

[b] *Polymer Institute, Slovak Academy of Sciences, 842 36 Bratislava (Czechoslovakia)*

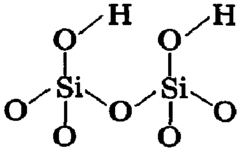
(Received June 13, 1986)

Summary

The photolysis of the suspension benzaldehyde solution in *n*-heptane–silica gel has been studied by UV absorption spectroscopy and thermal gravimetry. The formation of surface esters, oligomers and polymers during irradiation is proposed on the basis of the results obtained. Significant lowering of the silica-gel surface hydrophilicity is found after UV irradiation in the presence of benzaldehyde.

1. Introduction

The chemical reactivity of various forms of solid silica is determined primarily by the nature of their surface properties. The so-called excess valences arising from the interruption of the crystal lattice periodicity on the interface act as active sites for reactions with molecules in the atmosphere [1, 2]. Under normal conditions these sites are immediately hydrated and the so-called silanol surface is formed [3]:



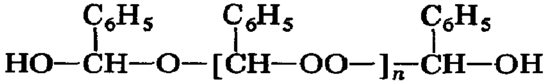
The silanol surface possesses a strong hydrophilic character and yields chemisorption reactions when in contact with various inorganic and organic compounds [3 - 5]. Chemisorption reaction lowers or even eliminates the hydrophilicity of the silica surface and has been frequently investigated. The chemisorption of organosilicon compounds [6 - 9] and surface etherification and esterification by organic alcohols [3, 4], acids [4, 10 - 12] and organic acid derivatives [4] have been studied as methods for lowering the hydrophilicity of the silica surface.

[†] Dedicated to Professor Dr. Alexander Tkáč, DSc., of the Slovak Technical University, Bratislava, on the occasion of his 65th birthday.

0047-2670/87/$3.50

Photochemically initiated chemisorption on the silanol surface has been given relatively little attention. It has been found that both active surface adsorption sites [13] and surface free radicals [14] are formed during short-wavelength UV irradiation. Ševec [15] found that aryl radicals are formed and chemisorption rises during irradiation of aromatic compounds adsorbed on silica gel.

The photolysis of benzaldehyde has been studied in the gas phase and in the liquid. Irradiating at a wavelength of about 270 nm causes the cleavage of gaseous benzaldehyde to give benzene and carbon monoxide by a molecular mechanism [16]. A yellow polymer was formed as a result of the $n \rightarrow \pi^*$ excitation of the gaseous benzaldehyde [16]. Although neither the detailed polymerization mechanism nor the product structure has been elucidated, a radical polymerization initiated by excited benzaldehyde has been proposed. The products of benzaldehyde photolysis in solution are benzoin and hydrobenzoin, and a radical pathway with $(C_6H_5\dot{C}HOH)$ and $(C_6H_5\dot{C}O)$ radicals as the primary intermediates has been proposed for this photoreaction [17 - 19]. If the photolysis is carried out in the presence of oxygen, the primary radicals are oxidized to peroxo radicals [20 - 23], and the products of benzaldehyde photo-oxidation are peroxobenzoic and benzoic acids and oligomeric compounds of the type



$$\mathrm{HO{-}\overset{C_6H_5}{\overset{|}{C}}H{-}O{-}[\overset{C_6H_5}{\overset{|}{C}}H{-}OO{-}]_{n}{-}\overset{C_6H_5}{\overset{|}{C}}H{-}OH}$$

I

2. Experimental details

The benzaldehyde solution–silica gel suspension was irradiated in the device illustrated in Fig. 1. The radiation source (a medium pressure mercury lamp RVL-400 without luminophore, Tesla Holešovice, C.S.S.R.) and the quartz reaction vessel were placed at the focus point of an elliptical body with a reflecting inner surface. The silica gel (for chromatography, 5/40 μm, Lachema, C.S.S.R.) was dried for 3 h under vacuum at 90 °C. Benzaldehyde (Reachim, U.S.S.R.) was purified with an aqueous solution of Na_2CO_3 after separation of the water layer, dried with anhydrous Na_2SO_4, filtrated and distilled at 2.6×10^3 Pa and 81 °C. *n*-Heptane (for UV spectroscopy, Lachema, C.S.S.R.) purified with anhydrous $CuSO_4$ and cyclohexane (for UV spectroscopy, Lachema, C.S.S.R.) was used for the preparation of the solutions and suspensions.

The silica gel (200 mg) was stirred for 1 h in 70 cm^3 benzaldehyde solution in *n*-heptane. This length of time was found to be sufficient to establish the adsorption equilibrium. After the silica gel had settled, a sample of the solution was analysed spectrophotometrically at a wavelength of 240 nm and the equilibrium benzaldehyde concentration was determined. The suspension was transferred to the reaction vessel and was irradiated

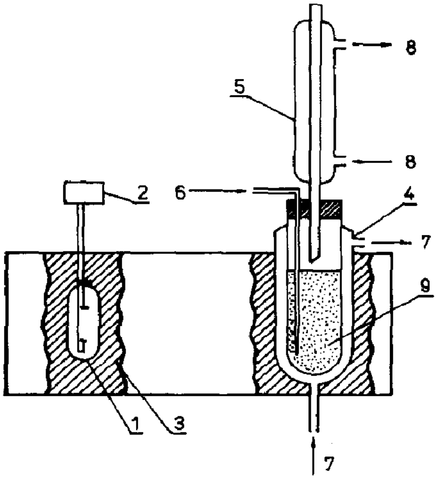


Fig. 1. Schematic diagram of irradiation device: 1, irradiation source; 2, power supply; 3, reflecting body; 4, reaction vessel; 5, reflux condenser; 6, oxygen inlet; 7, water for temperature control; 8, cooling water; 9, suspension.

for a fixed period at 20 °C. During irradiation, oxygen was bubbled into the suspension. After irradiation the silica gel was repeatedly washed in *n*-heptane and dried to constant weight at 40 °C under vacuum.

The samples of silica gel were studied by UV absorption spectroscopy, thermogravimetry (TG) and derivative thermogravimetry (DTG). The hydrophilicity of the samples was determined by measuring the absorption of water vapour.

The samples for UV spectroscopy were prepared according to the method of Leemakers *et al.* [24]. The silica gel was weighed out into a standard quartz cuvette of thickness 1.1 cm and was covered with cyclohexane. As the values of the refractive indices of silica gel (1.43) and cyclohexane (1.42) are similar, the resulting suspension is practically transparent in the UV region [25, 26]. The spectra were recorded on a SPECORD UV–visible spectrophotometer (C. Zeiss, G.D.R.).

TG and DTG curves were recorded on a 2 FA Thermoanalyzer (Mettler). A flow of purified nitrogen of 7 dm^3 min^{-1} and dynamic heating at 10 °C min^{-1} were employed and freshly burnt Al_2O_3 was used as the standard.

Measurements of water vapour adsorption were performed in an atmosphere with a saturated water vapour pressure of 2226 Pa (97% humidity). The amount of the water adsorbed on the sample surface was evaluated in periods of 5 - 10 min by measuring the relative increase in the weight of the sample.

3. Results and discussion

The absorption bands in the UV spectrum of benzaldehyde adsorbed on silica gel (Fig. 2) are broader than the bands in the spectrum of the solution

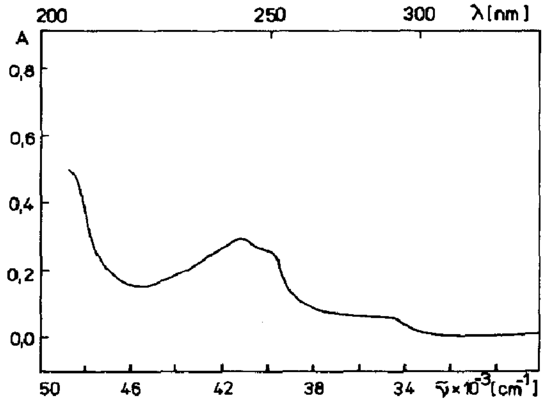


Fig. 2. UV spectrum of benzaldehyde adsorbed on silica gel (equilibrium benzaldehyde concentration, 4×10^{-5} mol dm^{-3}).

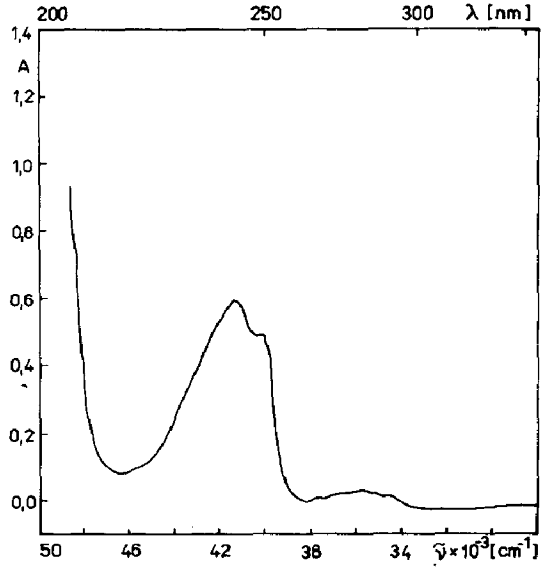
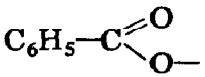


Fig. 3. UV spectrum of 3.8×10^{-5} mol dm^{-3} benzaldehyde in *n*-heptane solution.

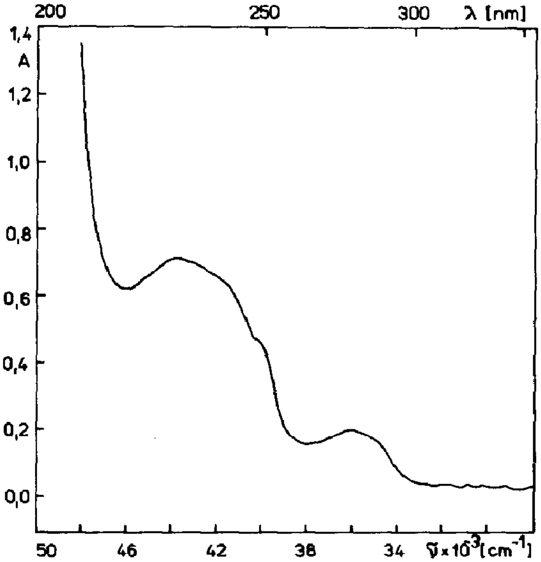
(Fig. 3). This broadening originates from the various adsorption states of benzaldehyde on the silica-gel surface. The maxima of the $\pi \rightarrow \pi^*$ transitions are at the same wavelengths in both spectra, so the electronic structure of the benzaldehyde remains unchanged on adsorption. Therefore it may be concluded that benzaldehyde is bonded to the silica gel surface by van der Waals forces supplemented to a certain extent by interactions of the surface silanols with the carbonyl oxygen. It is interesting to note that according to Sidorov [27] the IR absorption of the benzaldehyde C=O group is shifted only 6 cm^{-1} after it is adsorbed on porous glass.

After irradiation for 1 h (equilibrium concentration of benzaldehyde in the suspension, 4×10^{-5} mol dm^{-3}) a new band appears at about 230 nm (Fig. 4). After irradiation for 3 h the UV absorption of benzaldehyde on silica gel completely disappears (Fig. 5), so the electronic structure of the surface-bonded molecule is different from that before photolysis. Its UV spectrum is characteristic of the group



$C_6H_5{-}C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow O-}$

TG and DTG curves of the initial silica gel and of that after irradiation in benzaldehyde solution (equilibrium concentration of benzaldehyde in the suspension, 4×10^{-5} mol dm^{-3}) are shown in Fig. 6. There is a decrease in weight at 50 - 150 °C from the distillation of bonded water, and from Fig. 6 it is evident that the water content is significantly lower in the irradiated samples. Further weight decreases resulting from the thermolysis of the surface structure at 250 - 320 °C and 350 - 500 °C were recorded only for the irradiated samples.



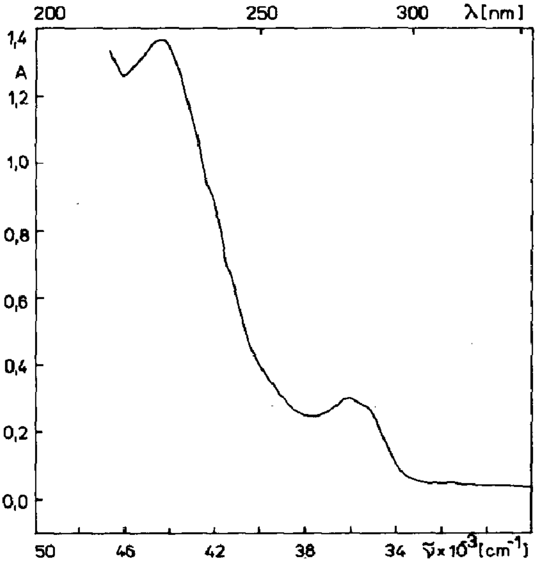


Fig. 4. UV spectrum of silica gel after 1 h irradiation in benzaldehyde solution (equilibrium benzaldehyde concentration, 4×10^{-5} mol dm^{-3}).

Fig. 5. UV spectrum of silica gel after 3 h irradiation in benzaldehyde solution (equilibrium benzaldehyde concentration, 4×10^{-5} mol dm^{-3}).

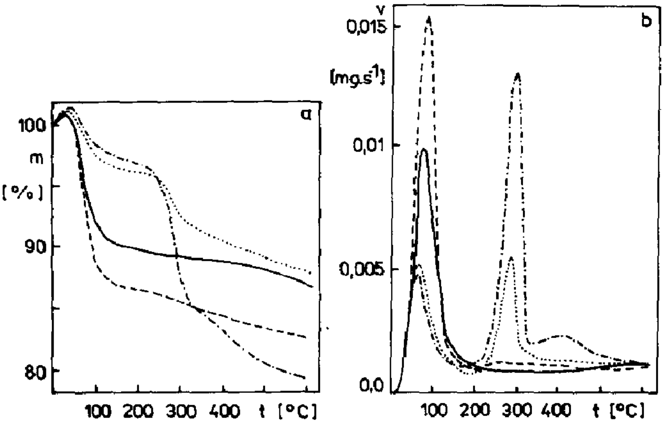


Fig. 6. (a) TG and (b) DTG curves of silica gel treated in benzaldehyde solution (equilibrium benzaldehyde concentration, 4×10^{-5} mol dm^{-3}): ——, untreated silica gel; — — —, without irradiation; ·······, 1 h irradiation; — · —, 3 h irradiation.

As the oxygen was contained in the solvent and on the silica-gel surface, photo-oxidation reactions of benzaldehyde took place during the irradiation of the system under study. The main primary product, *i.e.* the unstable peroxobenzoic acid [20, 21], is able to oxidize benzaldehyde to benzoic acid [28]. The TG and DTG curves of silica gel treated with a solution of benzoic acid in *n*-heptane (equilibrium concentration of benzoic acid, 4×10^{-5} mol dm^{-3}), in the same way as with the previous samples but without irradiation, are qualitatively consistent with untreated silica-gel

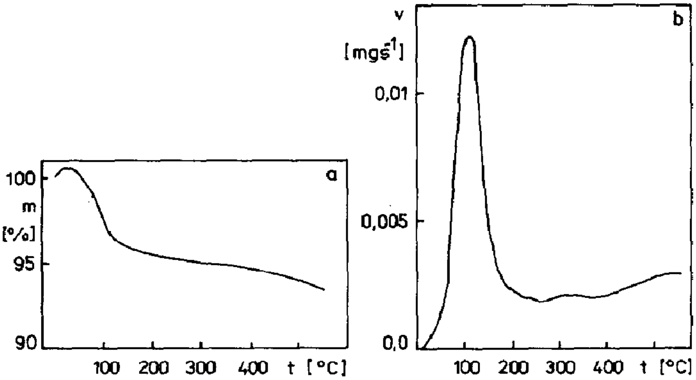
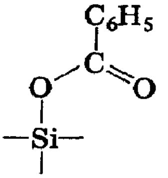


Fig. 7. (a) TG and (b) DTG curves of silica gel treated in benzoic acid solution (equilibrium benzoic acid concentration, 4×10^{-5} mol dm^{-3}).

curves (Fig. 7). Therefore the physically adsorbed benzoic acid did not cause the observed changes on the TG and DTG curves for the irradiated samples.

With regard to the UV absorption spectra and to the TG and DTG curves of silica gel photolysed in benzaldehyde solution, the existence of aromatic structures (probably surface esters) chemically bonded to the silica-gel surface may be presumed:



Analogous changes in the UV spectra, such as those shown in Figs. 4 and 5, were observed after irradiation of suspensions with a benzaldehyde equilibrium concentration of up to 5×10^{-3} mol dm^{-3}. Photolysis of suspensions with a higher benzaldehyde equilibrium concentration caused the silica gel to become tawny coloured and its UV absorption bands were greatly broadened (Fig. 8). This broadening may be connected with the chemical nature of the surface structures being different from that of the structure present in suspensions with a lower benzaldehyde concentration. A higher concentration of benzaldehyde favours surface oligomerization, leading to type I products or even to photochemical polymerization of benzaldehyde [16].

The rate of water vapour adsorption on the solid surface can be described to a first approximation by the first-order equation

$$a(t) = A\{1 - \exp(-kt)\}$$

where $a(t)$ is the amount adsorbed during the period t, k is the first-order rate constant and A is the amount adsorbed in the saturated state. The parameters A and k for the adsorption of water vapour on the silica-gel

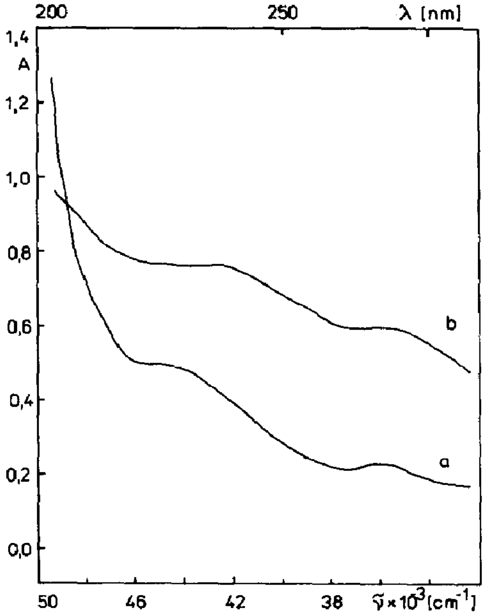


Fig. 8. UV spectra of silica gel after irradiation for 5.5 h in benzaldehyde solution: (a) equilibrium benzaldehyde concentration, 1×10^{-2} mol dm^{-3}; (b) equilibrium benzaldehyde concentration, 3.5×10^{-2} mol dm^{-3}.

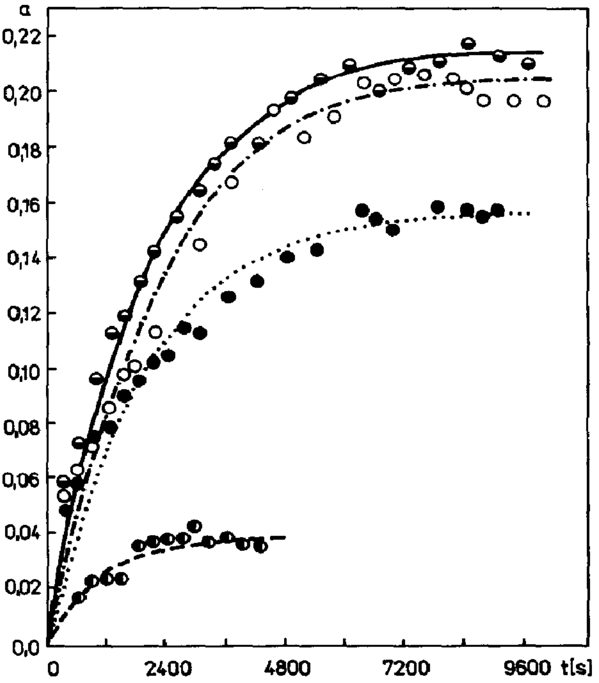


Fig. 9. Water vapour adsorption on silica gel treated in benzaldehyde solution (equilibrium benzaldehyde concentration, 4×10^{-5} mol dm^{-3}): ◓, untreated silica gel; ○, without irradiation; ●, 1 h irradiation; ◐, 3 h irradiation.

TABLE 1

Amount of water adsorbed on the silica-gel samples in the saturated state

Equilibrium benzaldehyde concentration in suspension (mol dm^{-3})	*Period of irradiation* (h)	*A*
Non-treated silica gel		0.215
4×10^{-5}	0	0.205
4×10^{-5}	1	0.156
4×10^{-5}	3	0.037
1×10^{-2}	5.5	0.098
3.5×10^{-2}	5.5	0.084

samples were evaluated by non-linear regression [29]. According to Fig. 9 and Table 1 the capacity of the silica-gel surface to adsorb water vapour is significantly reduced after irradiation in benzaldehyde solution, so its hydrophilicity is decreased.

Acknowledgments

We would like to thank Dr. B. Reiser and Dr. I. Šurina (Department of Textile, Pulp and Paper, Slovak Technical University) for performing the TG and DTG measurements.

References

1 F. Haber, *Z. Elektrochem.*, *20* (1914) 521.
2 I. Langmuir, *J. Am. Chem. Soc.*, *40* (1918) 1361.
3 R. K. Iler, *The Chemistry of Silica*, Vol. 2, Wiley-Interscience, New York, 1979.
4 M. L. Hair, *Infrared Spectroscopy in Surface Chemistry*, Dekker, New York, 1968.
5 V. V. Strelko and V. A. Kanabolockij, *Kolloidn. Zh.*, *33* (1971) 750.
6 I. Y. Neimork, *Neftechimija*, *3* (1963) 149.
7 K. Veselý, *Chem. Listy*, *71* (1977) 225.
8 W. Hertl and M. L. Hair, *J. Phys. Chem.*, *75* (1971) 2181.
9 H. H. Hsing and A. C. Zetllemoyer, *Prog. Colloid Sci.*, *61* (1976) 54.
10 J. Fraissard and R. Caillat, *J. Chim. Phys.*, *60* (1963) 1017.
11 K. Marshall and C. H. Rochester, *J. Chem. Soc., Faraday Trans. I*, *71* (1975) 1754.
12 R. P. Eischens, *Science*, *146* (1964) 486.
13 K. G. Krasilnikov, V. F. Kiselev and E. A. Sysojev, *Dokl. Akad. Nauk SSSR*, *116* (1957) 990.
14 H. P. Boehm, *Adv. Catal.*, *16* (1966) 226.
15 D. I. Ševec, *Adsorpcija i Adsorbenty*, Tom. 1, Naukova Dumka, Kiev.
16 M. Berger, I. L. Goldblatt and C. Steel, *J. Am. Chem. Soc.*, *95* (1973) 1717.
17 M. Cocivera and A. M. Trozzolo, *J. Am. Chem. Soc.*, *92* (1970) 1772.
18 G. L. Clos and D. R. Paulson, *J. Am. Chem. Soc.*, *92* (1970) 7229.
19 P. G. Frith and K. A. McLauchlan, *J. Chem. Soc., Faraday Trans. II*, *71* (1975) 1984.

20 H. L. J. Bäckstrom and U. Rüner, *Acta Chem. Scand.*, *20* (1966) 630.
21 H. L. J. Bäckstrom, U. Rüner and C. F. Åquist, *Acta Chem. Scand.*, *20* (1966) 645.
22 H. L. J. Bäckstrom and C. F. Åquist, *Acta Chem. Scand.*, *24* (1970) 1431.
23 J. S. Bradslaw, R. D. Kundsen and W. W. Parish, *J. Chem. Soc., Chem. Comm.*, (1972) 1321.
24 P. A. Leemakers, H. T. Thomas, L. D. Weis and F. C. James, *J. Am. Chem. Soc.*, *88* (1966) 5075.
25 M. Robin and K. N. Trueblood, *J. Am. Chem. Soc.*, *79* (1957) 5138.
26 D. Fassler, R. Gade and W. Guentler, *J. Photochem.*, *13* (1980) 49.
27 A. N. Sidorov, *Zh. Fiz. Chim.*, *30* (1956) 995.
28 K. Tokumaru and M. Fukuyama, *Bull. Chem. Soc. Jpn.*, *35*, (1962) 1873.
29 F. Irman, in *Proc. II Seminar of EMG 666 Calculator Users*, Czechoslovak Metrological Institute, Bratislava, 1983, p. 423.