Percutaneous absorption of methyl methacrylate by dental technicians

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Acrylic plastics are in common use in prosthetic dentistry.¹ Clinical¹ and experimental evidence² indicates that the most common monomer used, methyl methacrylate, is absorbed through the skin and can produce neurological effects.¹ Free methyl methacrylate may be found in blood after the endoprostheses of the hip.³

Biological monitoring of occupational exposure has never been reported. The methyl ester of the methacrylic acid ester is broken down in the body and the free acid enters the tricarboxylic acid cycle after conjugation with the coenzyme A. This complex is a normal intermediate in the valine metabolism.^{4,5} Another pathway is through conjugation with glutathione.⁶

We have analysed urinary methacrylate as an index of percutaneous absorption in 11 dental technicians during an ordinary working day.⁷

Subjects and methods

Eleven dental technicians participated in the study on a voluntary basis. Most had been contacted in an earlier clinical study¹ and they were willing to collect 24 hour urine specimens. The collection started Thursday morning with the first urine and ended on the first Friday morning urine. The second urine sample on the Friday morning just before work constituted the Friday reference sample. All voided urine was retained and its volume was measured: 0.5 ml of concentrated sulphuric acid were added to 5 ml of urine. The acidified urine was extracted three times without delay in 20 ml of diethyl ether. The extracts were combined and dried over anhydrous sodium sulphate. The ether was then evaporated to near dryness and 1 ml of a mixture of 1,1,1-trichloroethanol and trifluoroacetic anhydride (1:2, v/v) with two drops of concentrated orthophosphoric acid was added.⁸ The mixture was incubated for 30 minutes at 115°C. After cooling, 10 ml of methyl *t*-butyl ether were added, and after shaking the organic phase was recovered and excess

reagents removed with saturated sodium bicarbonate solution. The trichloroethyl methacrylate ester was analysed by gas chromatography (Hewlett-Packard model 5790A) equipped with a capillary column and a ⁶³Ni electron capture detector operated at 320°C. The splitless injection mode was used with a temperature programme as follows. The rate of 25°/min was maintained between 60° and 200°C and the latter was kept for 18 minutes. The retention time of the ester with this programme was 20.8 minutes. The standard methyl methacrylate trichloroethyl ester was of our own synthesis and it was purified on silica plates with acetone/nitrile dichloromethane mixture (20:80, v/v) as an eluent. The recovery in the extraction and analysis for the urinary methacrylate was 99% with a detection limit at—0.5 µmol/l. Urinary creatinine was analysed with the alkaline picric acid method.⁹

Results and discussion

The urinary methacrylic acid levels showed a large variation (table), probably reflecting exposure rather than differences in the valine metabolism of the subjects as low methacrylate concentrations were

Urinary output of methacrylate by dental technicians exposed to methyl methacrylate

Subject	Time exposed (min)	Excretion (nmol/24h)	Highest concentration (nmol/mmol creatinine)	Preshift concentration (nmol/mmol creatinine)
1	30	122	122	9
2	60	200	373	6
3*	30	122	55	ND
4†	120	30	16	ND
5†	240	93	64	30
6†	30	19	35	ND
7†	30	20	27	ND
8*†	30	34	35	24
9*	30	84	85	15
10*	180	54	22	ND
11*	180	59	56	6

*Used protective cream.

†Current dermatitis.

ND = Not detectable (detection limit—0.5 nmol/l).

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found in the urine samples before work. The subjects described the study period as a "normal" day, although they did not time the tasks which involved manual contact with the liquid monomer except in terms of total time. The times varied from 30 minutes to four hours but the chores were probably scattered throughout the working period as there was no consistent pattern in the highest urinary methacrylate concentration in relation to the time of day. This might have been caused by the delay in passing the skin barrier. It is often proposed that diseased skin is a less good barrier than healthy tissue. The urinary methacrylate, however, correlated poorly with current dermatitis (table). It seems that the use of protective gels or creams provides only a relative protection (table).

Methacrylate has not been found in the urine of healthy controls.^{10,11} The low methacrylate levels in the morning urine and in controls (always <15 nmol/mmol creatinine, n = 10) are compatible with published data, although their origin are unclear. The control concentrations were, however, considerably lower than those excreted by the technicians.

These 24 hour urine samples collected over a working day show percutaneous absorption of methyl methacrylate to have occurred. The ambient vapour concentrations in the dental work are so low¹² that they cannot be a source of the urinary methacrylic acid.

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