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HIGH-PERFORMANCE LIQUID CHROMATOGRAPHIC DETERMINATION OF BENZIL IN AIR AS AN INDICATOR OF EMISSIONS DERIVED FROM POLYESTER POWDER COATINGS

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SUMMARY

A method to estimate occupational exposure to emissions from the curing of polyester powder paints was developed. The method is based on the monitoring only of a certain marker compound in workroom air in order to make the determinations easier. Benzil, reproducibly emitted from all the powders tested, was chosen as the indicator for curing (220°C)-derived emissions. A method for the air sampling and high-performance liquid chromatographic benzil is described. Aspects of the use of marker compounds are discussed.

INTRODUCTION

The industrial hygiene aspects of powder coating treatments have been studied in our laboratory for some years. The principle of measuring certain marker compounds only was adapted to enable estimations of powder-related occupational health risks. Previous studies were concerned with epoxy resin based powder coatings[1,2]. These studies have since been extended to include polyester-based powder coatings, the second most popular powder material in use in Finland.

The purpose of this study was to choose a suitable indicator from among the compounds released during the thermal curing of several commercial polyester powder coatings. The existence of a marker in workroom air is a sign of emissions into that air and thus a measure of air quality.

Laboratory curing experiments were performed in the search for a marker which is reproducibly emitted at the curing temperatures. Benzil proved to be a suitable marker, and has been analysed by gas–liquid chromatography (GLC)[3,4] and high-performance liquid chromatography (HPLC)[5]. There are, however, no literature data on the air sampling of benzil. In this paper we propose a method for the air sampling of benzil and for its liquid chromatographic determination. Air samples were collected on combinations of 13-mm glass fibre filters and silica sorbent tubes and were analyzed by HPLC with UV detection.

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EXPERIMENTAL

Laboratory curing of powders

Three commercial polyester coating powders were cured in laboratory experiments. The compounds released were collected and chromatographed with GC to obtain the corresponding emission profiles. Curing experiments were carried out with a device based on a movable oven system, described elsewhere[6]. A 10-g amount of powder was spread over a length of 100 cm in a glass tube (1500 mm x 17 mm I.D.). An oven was moved along the tube at 1 cm/min. The oven temperature was set at 220°C which is a typical curing temperature for polyester powders. Synthetic air (20% oxygen, 80% nitrogen) was drawn through the tube at 500 ml/min.

A 37-mm glass fibre filter (Sartorius, Cat. No. SM13400) in a 37-mm filter holder was connected to the outlet of the sample tube by PTFE tubing. A spiral glass cold trap was connected after the filter to collect the volatiles, and was cooled with solid CO_2. After sampling, the filter was extracted in a test-tube with 2.0 ml of dichloromethane. The contents of the spiral trap were eluted with 1.0 ml of dichloromethane.

Selection of the marker

The air samples in dichloromethane from the curing experiments were concentrated to 200 μl and 1.5 μl were injected into an Hewlett-Packard 5790A gas chromatograph equipped with a flame ionization detector and operated in a splitless mode. The compounds emitted were separated with a BP-5 fused-silica column (25 m × 0.22 mm I.D.: SGE, Australia) with a 0.25-μm film. The peaks of interest were identified with a Hewlett-Packard 5890 gas chromatograph equipped with an HP 5970 mass-selective detector. The temperature programme started from 30°C held for 1 min and reached 275°C in 55 min.

Air sampling of benzil

Air atmospheres containing benzil were produced to test the sampling performance of 13-mm glass fibre filters and silica air sampling tubes connected together or separately. Benzil or powder materials were placed in the bend of a J-shaped glass tube (300 mm × 5 mm I.D.) which was inserted in a laboratory oven. The J-tube was heated at 220°C. No attempt was made to make the vaporization linear. The outlet arm of the J-tube was connected to a 1-l empty impinger bottle which was connected

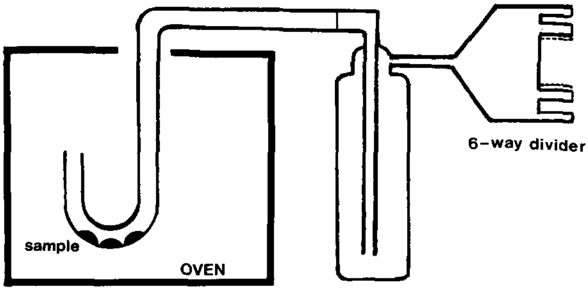

Fig. 1. A schematic diagram of the J-tube assembly.

to a six-way glass divider for simultaneous comparisons between different collection media. A schematic diagram of the J-tube assembly is shown in Fig. 1. Rather spacious glass tubing was utilized for reasons of conditional similarity for the laboratory and workroom sampling. The purpose was to allow cooling of the air stream before sampling better to simulate the sampling conditions in a workroom. However, this experimental set-up subjected benzil to severe adsorption on the walls of the apparatus.

Two filter cassettes containing the filters were connected in series. The filters (13 mm, Type AE, Cat. No. 225-16; SKC, Eighty Four, U.S.A.) were analyzed separately, as were the analytical and back-up sections of the silica tubes (70 mm x 6 mm, 150/75 mg packing, Cat. No. 226-10, SKC). Air was drawn through each arm of the six-way system by personal air-sampling pumps (Model 222-3, SKC) at the rate of 200 ml/min.

Desorption tests

The desorption of benzil from the 13-mm filters was studied by injecting 30 μl of standard solutions of benzil in methanol onto the filters. The filter loadings were 0.1, 0.2 and 0.5 μg. The filters were allowed to dry and were then immersed in 1.0 ml of methanol. Desorption from the silica tubes was studied by adding the content of a tube to 1.0 ml of a standard methanol solution. The concentrations of these solutions were 0.2, 0.5 and 1.0 μg/ml. Overnight phase equilibration for both types of samples was carried out before analysis.

Liquid chromatography

Air samples of benzil were analyzed with a Pye Unicam Model 100A liquid chromatograph equipped with a Pye Unicam LC-XP gradient programmer and a Shimadzu SPD-6A UV detector operated at 260 nm. The column was a Spherisorb ODS^{-2} (5 μm, 150 mm × 4.6 mm I.D.; Phase Separations, U.K.). The mobile phase was water–methanol (40:60), flow-rate 1.0 ml/min. External standards in methanol were made from 98% pure benzil (Cat. No. B515-1, Aldrich).

RESULTS AND DISCUSSION

Air samples collected on the 37-mm filter and cold trap from the laboratory curing experiments were subjected to GC to obtain the emission profiles. The curing experiment was repeated twice for each powder material. The two emission profiles of a particular polyester coating material were very similar. Fig. 2 shows a chromatogram of a curing air sample. Gas chromatograms of the three coating materials were investigated to find common peaks in all of them. The filter sample contained high-boiling compounds while the more volatile fraction of the emissions was found in the cold trap.

A marker compound should preferably not be a common contaminant found in industrial environments like formaldehyde or phthalates. A marker should also be present in the emissions at concentrations exceeding trace level to enable convenient field sampling times. The marker emissions should also be repeatable from experiment to experiment, indicating a constant emission mechanism.

In these experiments the peak corresponding to benzil fulfilled the aforemen-

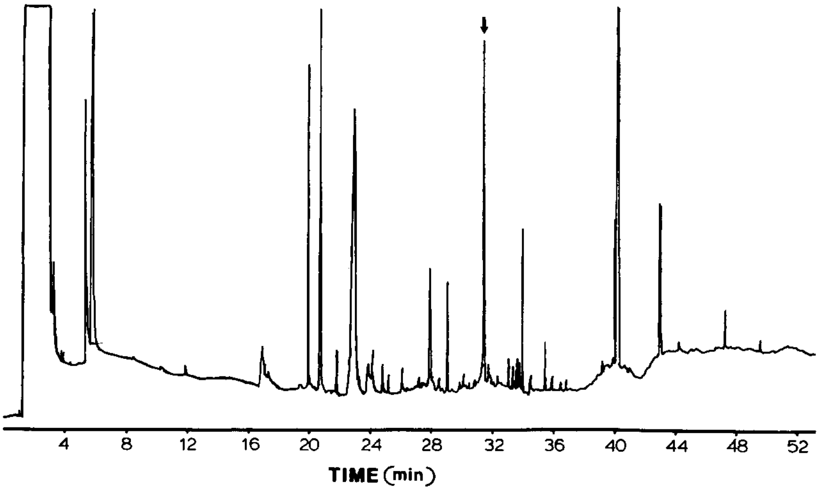

Fig. 2. A GC chromatogram of a curing air sample collected on a filter. The arrow points to the benzil peak.

tioned requirements. Benzil is probably used in polyester coating powders as an air release agent. It can thus be found also in uncured powders. The amounts of benzil in powders from different suppliers are comparable, making its use as a marker independent of the origin of the paint.

Benzil is a solid at ambient temperature and air sampling on filters is thus an obvious choice. The sampling characteristics of silica air-sampling tubes were, however, also tested. For simultaneous performance testing a six-way sampling train was employed. The benzil loading in the J-tubes was varied to give different benzil atmospheres. Adsorption on the walls of the long glass tubing preceding the collection area was considerable. This was considered irrelevant since the experimental conditions at the collection zone thus better represent the actual conditions in a workroom where the sampled air is at about room temperature, and the sample molecules to be collected typically have airborne residence times much longer than if sampled directly from the hot air stream coming from the outlet arm of the J-tube without the impinger bottle. The air concentration at the inlet zone of the collection media was estimated from the liquid chromatographic peaks of the 5-l samples by assuming 100% collection efficiency for the highest peak. These estimations are inaccurate but are indicative of the magnitude of the concentrations, and are referred to as apparent concentrations. The concentrations can not be estimated from the amount of the starting material in the J-tube because of the adsorption on the walls. Benzil was applied to the tube as methanol solutions of known concentrations which were allowed to dry before heating and sampling. The sampling efficiency was estimated by monitoring the amount of benzil found in the back-up sections or the second filter. The assumption was made that effective sampling occurred if the back-up sections remained clean.

The desorption efficiency of benzil into methanol from the collection media was determined before sampling experiments. The results for the silica and the 13-mm filters are shown in Table I. Methanol proved to be an efficient solvent for this purpose.

TABLE I

DESORPTION INTO METHANOL

R.S.D. = Relative standard deviation.

Standard solution (μg/ml)	*Recovery (%), mean ± R.S.D. (n=4)*		*Amount on filter (μg)*
	Silica	*Filter*	
0.2	100.6 ± 1.5	97.7 ± 1.9	0.1
0.5	99.5 ± 0.4	96.8 ± 0.8	0.2
1.0	100.9 ± 1.0	96.0 ± 0.5	1.6

From the air-sampling experiments it is evident that benzil exists at low concentrations in a form collectable more efficiently on sorbent tubes than on filters. A combination of filters and sorbent tubes is thus needed to cover a broad concentration range. The silica tubes we used have a 150-mg packing in the front section and a 75-mg packing in the rear. The fraction of benzil collected on filters is likely to represent that which is in the aerosol phase. The recoveries from the filters became increasingly larger than from the tubes with increasing air contamination. The aerosol formation in the sampling train is supposed to be roughly complete after such a long and voluminous sample path.

The sampling on filters and silica tubes or their combinations was examined with widely different J-tube loadings. The amounts recovered from each of the sections of the different sampling trains are shown in Table II. The results are the averages of two determinations. The total recoveries from the tubes, at the two lowest air concentrations, were larger than those from the filter. The order of collection efficiency was reversed at higher concentrations where the recovery from filters and filter-tube combinations becomes approximately equal, reflecting the low proportion of the gas phase component. A combination of a filter and tube is needed since the expected contamination levels in workroom air are at the lower end of the concentration range of this experiment. It is also noteworthy that the rear sections of the silica tubes in the combinations contained no benzil in all the tests performed. It is the cleanliness of the back-up sections that is considered a measure of the effectiveness of sampling. Low recoveries from the collecting media as a percentage of the starting material in the J-tube is not due to breakthrough but mostly due to adsorption on the walls of the tubing. Benzil was indeed recovered from the tubing walls by rinsing with methanol. However, quantitative analyses from the walls were not performed.

The effect of extended sampling time on recovery was also examined. Additional clean laboratory air was drawn through the sampling train after sampling the standard 5-l samples from the J-tube. It was shown that the additional sampling did not result in the appearance of benzil in the rear section of the tube. It seems that the gaseous fraction of benzil collected in the tube is effectively retained in the front section of the tube. The back-up section contained no benzil even after an additional clean air sampling of 48 l. However, benzil gradually disappeared completely from the filter during the extended sampling of clean laboratory air while the loading of the front section of the tube increased. Benzil seems to be evaporated or sublimed from

TABLE II

RECOVERIES FROM SILICA TUBES AND THEIR COMBINATIONS WITH THE FILTERS

Amount on J-tube (µg)	*Sample volume (l)*	*Recovery from the tubes and filters (µg)*					
156	5	Silica	front	1.55	Filter		0.48
			rear	–	Silica	front	0.60
						rear	–
	12				Filter		0.08
					Silica	front	0.96
						rear	–
	20				Filter	–	
					Silica	front	1.01
						rear	–
209	5				Filter		2.20
					Silica	front	2.41
						rear	–
	48				Filter		–
					Silica	front	4.32
						rear	–
256	5	Silica	front	2.08	Filter		5.29
			rear	0.17	Silica	front	1.13
						rear	–
522	5	Silica	front	11.37	Filter		23.43
			rear	1.21	Silica	front	1.21
						rear	–
1044	5	Silica	front	31.01	Filter		90.96
			rear	7.58	Silica	front	1.38
						rear	–

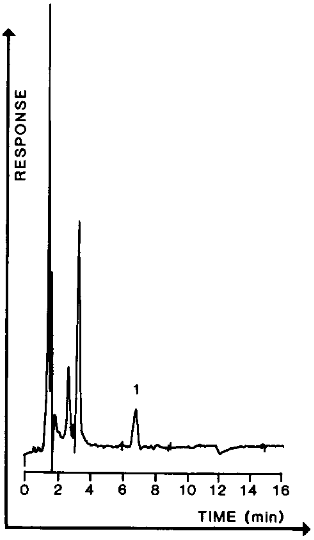

Fig. 3. An HPLC chromatogram of a curing air sample with about 80 mg of powder in the J-tube. The benzil peak (1) represents about 0.35 µg collected on the filter-tube combination or 7 ng injected for HPLC.

the filter when clean air is drawn through the filters and collected on the front section in the gas phase. The total amount of benzil recovered from the filter-tube combination did not alter significantly as a function of the additional sampling volume. A recovery of 93% was obtained (from the 5-l reference sample) after 4 h of additional clean air sampling from the tube combination. It appears that at least 48 l can be sampled at 200 ml/min. The sampling of clean air between contaminated atmospheres has a real-world basis because the emissions from the curing ovens are usually periodical, varying according to the amount of paint powder and/or the number of objects together with the processing conditions. The evaporation or sublimation of filter-bound solid material during extended sampling has been reported earlier[7,8].

The efficiency of the silica tube for collecting benzil in an essentially gaseous phase was tested by connecting the tubes directly to the outlet arm of the J-tube. As mentioned earlier, the experimental conditions hardly represent those of an actual workroom. The results would, however, be indicative of the ability of the tube to retain benzil in the gaseous phase. Samples were collected at 200 ml/min for 25 and 120 min corresponding to 5- and 24-l samples. Recoveries were 85–88% of the original J-tube loadings of 1 and 5 μg. Again the back-up sections of every tube contained no benzil. This indicates that at least 24 l of essentially gaseous atmospheres can be sampled, although the situation may be different when continuous atmospheres with linear evaporation rates are collected.

In the method we are proposing, benzil is determined with resersed-phase liquid chromatography using methanol–water (60:40) as the eluent. The UV detector is operated at 260 nm. The detection minimum giving a 1-cm peak is about 40 ng/ml corresponding to 0.85 μg/m^3 for a 48-l air sample. An HPLC chromatogram of an air sample obtained from an laboratory curing experiment is shown in Fig. 3. A major

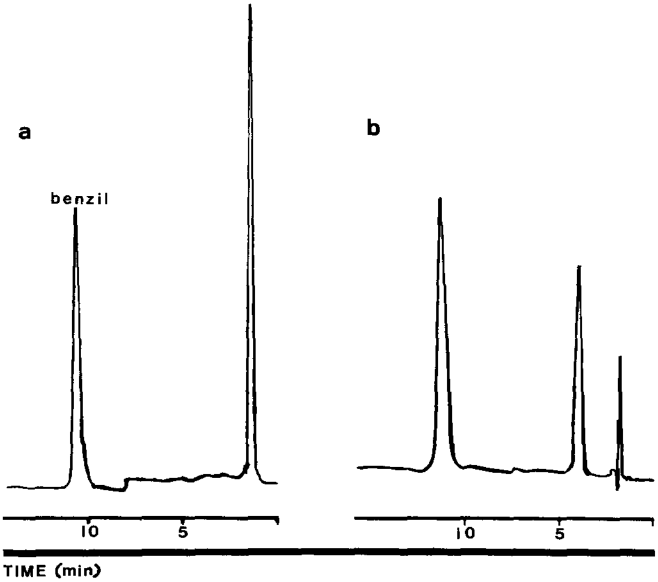

Fig. 4. An HPLC separation of benzil and benzilic acid. Eluents: (a) methanol–water (60:40); (b) methanol– 0.025 *M* KH_2PO_4 (60:40). pH 2.8 adjusted by orthophosphoric acid.

proportion of the compounds released during the curing process are more polar than benzil. Benzil can thus be well separated from the other emission components by reversed-phase chromatography.

Benzil is prone to form benzilic acid in a reaction known as the benzilic acid rearrangement. The stability of the standards in methanol was therefore monitored. Refrigerated but daily used standards were, however, stable over a period of at least 2 weeks. Standards stored on open shelves at room temperature gradually transformed mainly to benzilic acid over the same period of time. An HPLC separation of benzil and benzilic acid is shown in Fig. 4. Benzilic acid was not found in the air samples. We therefore believe that the action of sampling does not trigger the rearrangement reaction.

CONCLUSION

A method is described for the estimation of occupational emissions due to thermal curing of polyester powder coatings. The health effects of the emissions are caused by the combined action of the compounds present. It is therefore the emission levels rather than the concentrations of particular toxic compounds that are of interest. Emission levels are proportional to the concentration of a marker compound in workroom air. Benzil was selected as a marker for curing-derived emissions and is determined in the air by collecting it on combinations of 13-mm glass fibre filters and silica sorbent tubes. Air samples are analyzed by HPLC with UV detection.

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REFERENCES

1 J. Pukkila, K. Peltonen and T. Savolainen, *J. Chromatogr.*, 438 (1988) 443–446.
2 K. Peltonen and J. Pukkila, *J. Chromatrogr.*, 439 (1988) 375–380.
3 R. Schwartz and R. Mathews, *J. Chromatogr.*, 126 (1976) 113–116.
4 W. Brubaker and M. Ogliaruso, *J. Chromatogr.*, 324 (1985) 450–454.
5 M. Ross, D. Lines, K. Brain and R. Stevens, *Anal. Biochem.*, 87 (1978) 267–271.
6 K. Peltonen, *J. Anal. Appl. Pyrolysis*, 10 (1986) 51–57.
7 U. Knecht, C. Lämmler and S. Tobias, *Fresenius' Z. Anal. Chem.*, 326 (1987) 25.
8 J.-O. Levin, *Chemosphere*, 17 (1988) 671.