

Potentially Toxic Colorant Precursors and Preservatives Used in Finger-Paints

M. C. Garrigós, F. Reche, A. Jiménez

University of Alicante, Department of Analytical Chemistry, Post Office Box 99,
03080, Alicante, Spain

Received: 14 July 2000/Accepted: 11 February 2001

Finger-paints are paste and/or jelly-like colored preparations specially designed for children, directly applicable to suitable surfaces with fingers and hands. They essentially consist of, in addition to water, coloring agents, fillers, binders, humectants, preservatives, surfactants and embittering agents. Finger-paints, when compared to other toy products, present higher possibilities for significant risks for children, as the ingestion of the paint material and the possibility of intensive skin contact. Some aromatic amines as well as formaldehyde are among the additives mostly used in finger-paints manufacturing. Aromatic amines are used in finger-paints as colorants precursors, such in the case of azo dyes. These amines are potentially toxic and may present a mutagenic impact and carcinogenic activity (both in animals and humans) even at low concentrations (Gawdzik and Czerwinska-Bil 1991). The most common among these are 2-naphtylamine, 4-Cl-o-toluidine, benzidine and o-aminobiphenyl (Gupta 1991). Formaldehyde is normally used as a preservative (biocide) in finger-paints. Formaldehyde is a colorless gas at room temperature with piercing odor, high volatility and reactivity. Because of this high reactivity and versatility as a chemical intermediate, formaldehyde is considered a toxic substance, with irritant and local necrotic effects and potentially carcinogenic (Kirk and Othmer 1978).

Coloring agents and preservatives requirements have been set in European Standard prEN 71-7 (1999) for finger-paints. However, an analytical methodology to get a fast, reproducible and efficient determination of these compounds is lacking at the present time. One of the main problems associated to the reliability and reproducibility of the analysis is the extraction method. Some traditional extraction techniques such as Soxhlet have been used but with not good results. The interest in supercritical fluid extraction (SFE) as a extraction method has been growing rapidly during the last years. The application of SFE to the extraction of amines and formaldehyde, however, has been quite limited. Reliable methods to determine formaldehyde and aromatic amines based on SFE in finger-paints has been proposed by our research group. The aim of the present work is to study some of the commercial finger-paints present in the Spanish market to know if these toxic compounds are really used in formulations.

MATERIALS AND METHODS

Finger-paint samples were selected from those commercially available in Spanish toyshops. Reagent grade standards of 4-Cl-o-toluidine, 2-naphtylamine, 4-aminobiphenyl and benzidine were obtained from Sigma Chemical Co. (St. Louis, MO, USA). Stock solutions of each compound were prepared in methylene chloride (20 µg/g). Analytical grade methylene chloride and methanol were obtained from Normapur (Prolabo, Barcelona, Spain). All reagents for formaldehyde analysis were analytical grade and obtained from Panreac Química S.A. (Barcelona, Spain) and Normapur (Prolabo, Barcelona, Spain). A formaldehyde standard (38% w/v) was used to prepare all solutions that were standardized iodimetrically.

Infrared spectrophotometry was used for the characterization of the paints (Nicolet Magna-FTIR 550). Thermogravimetical analysis was also carried out with a Mettler TG-50 thermobalance, where the sample was run from 25 to 900 °C at 10 °C/min. A Phillips PW1480 X-ray spectrometer was also used.

SFE was performed (off-line mode) using an ISCO Model SFX-220 extraction system (Lincoln, NE, USA) consisting of SFX-220 extractor, SFX 200 controller and a 100DX-syringe pump. 0.2 g of sample were introduced in a stainless steel cartridge. SFE conditions were selected taking into account some previous studies about the optimization of the main variables involved in extraction to get the maximum efficiency and recovery of extracts.

For 4-Cl-o-toluidine, the selected conditions were 2000 psi, 120 °C, 15 min of static time, 15 min of dynamic time, 200 µl of methanol and 90 °C for the restrictor temperature. For the other amines (2-naphtylamine, 4-aminobiphenyl and benzidine) 8000 psi, 120 °C, 15 min of static time, 15 min of dynamic time, 80 µl of methanol and 105 °C for the restrictor temperature were used. In all cases, the modifier (methanol) was added directly to the cartridge before extraction. The outlet of the restrictor was immersed in a graduated dark vial with 10 ml of methylene chloride.

In the case of formaldehyde 100 µl of acetylacetone and 100 µl of an acetic acid-ammonium acetate buffer (pH 6.4) were added directly to the cartridge before extraction, to get the simultaneously derivatization and extraction of the analyte by the Hantzsch reaction (Nash 1953). 6580 psi, 104 °C, 15 min of static time, 15 min of dynamic time and 205 °C for the restrictor temperature were used. In order to trap the extracted analyte, the outlet of the restrictor was introduced in a double vial tandem with 5 ml of distilled water in each one. The final extract was then diluted to 15 ml.

Analysis of extracts to determine aromatic amines was carried out using a Shimadzu GC-17A (Kyoto, Japan) gas chromatograph equipped with a Shimadzu AOC-20i auto-injector, a TRB-5 capillary column (30 m long x 0.32 mm I. D.

with 0.5 μm film thickness) (Supelco, Bellefonte, PA, USA), a split-splitless injector and a flame ionization detector (FID). Chromatographic conditions were as follows: linear velocity of helium 70 cm/s and a head pressure of 153 KPa; injector and detector temperatures 300°C; column temperature from 70 °C (1.5 min) to 230 °C (3.5 min) at 12°C/min. 2 μl of sample were injected in the splitless mode.

The quantification of formaldehyde in SFE extracts with UV-V detection was carried out with a UV-1603 model Spectrophotometer (Shimadzu, Kyoto, Japan) using the absorbance at 410 nm of the 3,5-Diacetyl-1,4-dihydrolutidine formed in supercritical conditions.

Parameters of the proposed method, mainly limits of detection (LOD) and reproducibilities (RSD), were obtained for the five analytes studied. Results are presented in Table 1.

Table 1. Matrix main components from the studied finger-paints

Analyte	LOD (ng)	RSD (%)
4-Cl-o-toluidine	0.45	0.6
2-naphtylamine	0.64	1.3
4-aminobiphenyl	0.65	1.4
Benzidine	2.2	2.0
Formaldehyde	189	4.3

RESULTS AND DISCUSSION

Five different finger-paint samples were selected from those commercially available in toyshops, according to their different colors and their most extended use between children. Some tests for sample characterization were carried out in order to determine their main components. In this way, thermogravimetric analysis (TGA), infrared spectroscopy (FTIR) and X-ray fluorescence (XRF) made possible the determination of the percentage of volatile components for each paint, as well as their polymeric bases and fillers. The results are presented in Table 2, where each percentage is the average from all the paints of each analyzed type. As can be seen, the polymeric base was found to be Poly (vinyl alcohol) (PVOH) or Poly (vinyl acetate) (PVA) for all paints.

Table 2. Matrix main components from the studied finger-paints

Paint	Volatiles (%)	Polymer (%)	Filler (%)
A	64	PVOH (10)	Ca-Mg Silicate (18)
B	37	EVA (28)	CaCO ₃ (8); BaSO ₄ (20)
C	35	EVA (28)	Ca-Mg Silicate + BaSO ₄ (20)
D	33	PVOH (7)	CaCO ₃ (22)
E	33	EVA (31)	SiO ₂ (23)

PVOH: Poly(vinyl alcohol)

EVA: Poly(vinyl acetate:ethylene).

Different mineral fillers (talcum, calcium carbonate and silica dioxide) can be also found in the paints. It is surprising the big quantity of barium present in some samples, considering that this metal is under restrictions because of its potential toxicity for humans (European Standard EN 71-3 1996).

The presence of phthalate plasticizers in the paints was also studied by SFE and GC-FID analysis, using those conditions previously presented (Marín et al. 1996). The presence of DBP (Dibutyl phthalate) can be noted in paints E, as can be seen in Figure 1. In addition, paints A, B, C and D showed DEHP (Bis-(2-ethylhexyl) phthalate), but in always minor quantities. Plasticizers are normally used in paints to improve some of its properties as flexibility or processability. Although the presence of phthalate plasticizers in finger-paints is not restricted at this moment, the use of these plasticizers is being questioned worldwide because of their potential toxicity to humans (Menzel and Rohlfing 1990).

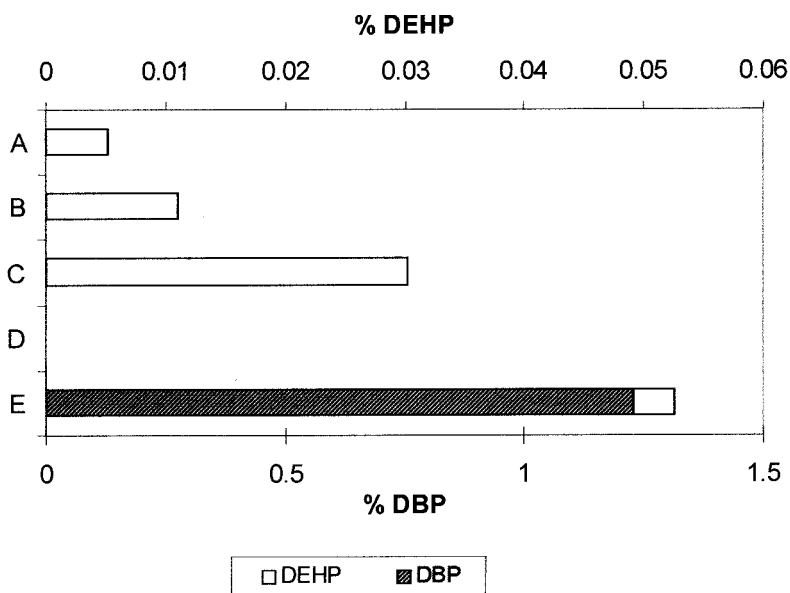


Figure 1. Phthalate plasticizers content found in finger-paints.

After characterization, the samples were extracted by SFE and the analytes studied (4-Cl-o-toluidine, 2-naphtylamine, 4-aminobiphenyl, benzidine and formaldehyde) were determined, using the above-indicated conditions. Recoveries for the optimum conditions were ranged between 76% and 91% in the case of 4-Cl-o-toluidine while were slightly lower for the other amines and formaldehyde. Twenty paints were tested, five of each type. Table 3 shows the results obtained, where the data are presented as amount of analyte per amount of sample. None of

the target compounds was detected in paints belonging to groups C, D and E, while different quantities of formaldehyde were found in paints A and B, being these quantities similar in all the paints belonging to the same group, and bigger for B paints compared with the A group. In all cases, the concentration of formaldehyde is smaller than the established in the European Standard prEN 71-7 for finger-paints (1000 mg/kg paint). Regarding to the four aromatic amines tested in this study, 4-Cl-o-toluidine was found in paints of group A, but 2-naphthylamine, 4-aminobiphenyl and benzidine were present at quantities lower than the LOD of the technique. Although this amine is found in a low concentration, its presence in finger-paints is forbidden by the prEN 71-7, attending to its very toxic character. This is the reason why these materials cannot be considered safe for children, and therefore some efforts should be made to eliminate this toxic amine. The amines are used as colorants precursors, and depending on the purity of raw materials and the integrity of the manufacturing processes these colorants may be contaminated by free potentially carcinogenic aromatic amines (Bürgi et al. 1997).

Table 3. 4-Cl-o-toluidine and formaldehyde contents in some finger-paints.

Paint	Group	Content (mg/kg paint)	
		4-Cl-o-toluidine.10 ⁴	Formaldehyde
1	A	2.15 ± 0.20	539 ± 67
2	A	1.24 ± 0.15	441 ± 38
3	A	1.68 ± 0.10	547 ± 53
4	A	2.22 ± 0.19	487 ± 49
5	B	< 0.01	793 ± 62
6	B	<0.01	756 ± 93
7	B	<0.01	764 ± 39
8	B	<0.01	742 ± 84

As can be seen, finger-paints present complex formulations containing several potentially toxic substances. No exhaustive control on these products has being applied until now; and for this reason, the use of reliable determination methods for these additives is advisable.

Acknowledgments. We thank the CICYT (Spain) (Project 1FD97-1080-C02) for their financial support.

REFERENCES

- Bürgi C, Bollhalder R, Otz T (1997) HPLC method for the determination of aromatic amines released from Water-colors under physiological conditions. Mitt. Gebiete Lebensm. Hyg 88: 305-320.
- CEN European Standard EN 71-3 (1996) Safety of Toys - Part 3: Migration of certain elements. European Committee for Standardization. Brussels, Belgium.

- CEN European Standard prEN 71-7 (1999) Safety of Toys - Part 7: Finger Paints - Requirements and test methods. European Committee for Standardization. Brussels, Belgium
- Garrigós MC, Reche F, Pernías K, Sánchez A, Jiménez A (1998) Determination of some aromatic amines in finger-paints for children's use by supercritical fluid extraction combined with gas chromatography. *J Chromatog A* 819: 259-266.
- Gawdzik B, Czerwinska-Bil U (1991) Porous copolymer-based cation exchanger for the off-line preconcentration of aromatic-amines from water. *Chromatographia* 32: 167-170.
- Gupta SP (1991) Discriminant analysis of carcinogenic nature of aromatic amines. *Indian J Chromatog.* 30B: 122-126.
- Kirk RE, Othmer DF (1978) *Encyclopedia of chemical technology*. 3th Ed. John Wiley & Sons, USA.
- Marín ML, Jiménez A, López J, Vilaplana J (1996) Analysis of poly(vinyl chloride) additives by supercritical fluid extraction and gas chromatography. *J Chromatog A* 750: 183-190.
- Menzel B, Rohlfing WH (1990) "Weichmacher". *Kunststoffe* 80: 810-815.
- Nash T (1953) The colorimetric estimation of formaldehyde by means of the Hantzsch reaction. *Biochem J* 55: 416- 421.