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Investigation of the Presence of Aniline in Chalk

Survey of chemical
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Preface

The project “Investigation of the presence of aniline in chalk” was carried out in from June till September 2017

This report presents analytical results of the determination of aniline in sidewalk chalk which potentially can be released from certain azo colorants or as free aniline originating from production. A broad spectrum of products was investigated.

The project was carried out by Danish Technological Institute.

The project was financed by the Danish Environmental Protection Agency.

Summary and Conclusion

The objective of this project was to investigate the likelihood of children being exposed to aniline when playing with sidewalk chalk. A recent investigation performed by Öko-Test formed the basis of this project, since it was claimed that red coloured chalk could contain or release aniline.

A total of 14 products of sidewalk chalk were collected from the Danish market. The red coloured chalk was subsequently selected for analysis. The content of aniline was determined according to the analytical standard EN71-7.

For 12 out of 14 products aniline was determined in concentrations below 5mg/kg in the red coloured chalk. This aniline exists either as free aniline or originates from azo-colorants contained in the chalk. For two products aniline could not be detected.

Sammenfatning og Konklusion

Formålet med dette projekt var at undersøge, hvor sandsynligt det er, at børn eksponeres for anilin, når de leger med fortovskridt. En ny undersøgelse fra Öko-Test danner grundlaget for projektet, idet undersøgelsen hævder, at rødt fortovskridt kan indeholde eller frigive anilin.

I alt 14 forskellige slags fortovskridt blev indkøbt på det danske marked. Dernæst blev det røde fortovskridt analyseret. Indholdet af anilin blev bestemt iht. Standard EN71-7.

I 12 ud af de 14 produkter blev anilin bestemt i det røde fortovskridt i koncentrationer under 5 mg/kg. Denne anilin findes enten som fri anilin eller kan frigives fra azofarvestoffer indeholdt i fortovskridtet. 2 af produkterne viste intet indhold af anilin.

1. Sidewalk Chalk

Most chalks contain pigments/colorants with different colours. A group of colorants called azo-colorants are produced from primary amines such as aniline. Under certain conditions, they may decompose and thereby release smaller compounds such as aniline. A recent investigation performed by Öko-Test claimed that red coloured sidewalk chalk could contain or release aniline. This investigation uncovers whether or not chalk purchased on the Danish market contains aniline or could release this substance through the degradation of azo-colorants.

1.1 Purchase of chalk

Sidewalk chalk is easily available in a variety of stores at low cost. The stores include toy shops, hobby stores, discount chain shops and DIY retailers. Altogether, 14 different products were bought in these stores. In general, the products were available in packages of three or more pieces and they come in various sizes.

The number of distributors were less than the number of products. Two products that looked different and were bought in different stores had the same distributor.

The price of most the purchased products was in the range of DKK 10-25 for one package. Two products were found to be more expensive and cost DKK 40 and 60, respectively. They were bought in a toy store.

All products are labelled with the CE marking. One product was labelled with EN71-7.

1.2 Selection of red chalk for testing

Sidewalk chalk exists in a variety of colours that vary in intensity. Red was the preferred choice of colour, since the results presented by Öko-Test showed that aniline is released from red coloured chalk. All purchased products contained at least one red coloured chalk. Therefore, the red coloured chalk was chosen for analysis of aniline.

It was observed that the intensity of the colour of the chalk varied. This variation was also observed for one product in the store, and the package of chalk with the most intensive colour was chosen.

2. Determination of Aniline

Aniline is a primary aromatic amine, which is used for the production of azo colorants widely used as dyes. Decomposition of these colorants can cause the release of aniline. In addition, any aniline present in toys such as sidewalk chalk may originate from the production. Aniline originating from production is referred to as free aniline. The methods of analysis can be chosen in order to distinguish between free aniline or aniline originating from azo colorants.

2.1 Quantitative determination of aniline

The analytical standard EN71-7 is used to determine a variety of primary aromatic amines including aniline in finger paint. The standard includes two types of sample preparation that allows to distinguish between free aniline or aniline originate from azo-colorants.

The standard EN71-7 was chosen for the quantitative determination of aniline in chalk due to the resemblance between finger paint and chalk as test material. The method highly resembles the standard DIN EN 14362-1 referenced by Öko-Test, which describes determination of certain aromatic amines derived from azo colorants by reductive cleavage.

2.1.1 Aniline originating from azo colorants

The analytical method for determination of aniline that originates from azo colorants includes a reductive cleavage step during sample preparation. This means that azo-dyes are degraded and release primary aromatic amines, which are subsequently determined by gas chromatography with mass selective detection (GC-MS). Any aniline quantified by this method may originate from azo colorants but also includes any free aniline present.

In case of a positive result, it is not possible to conclude, which type of azo-dye has been used in the chalk, due to limitations of the applied analytical method.

The reductive cleavage of azo colorants is not necessarily comparable to the degradation of these azo colorants when they are exposed to the skin or swallowed. Consequently, the analytical results are not suitable for the assessment of potential health hazards when children play with sidewalk chalk.

2.1.2 Free aniline

The method for determining free aniline does not include the reductive cleavage step, and any aniline present in the chalk is extracted and subsequently determined by gas chromatography with mass selective detection (GC-MS). Any aniline determined using this method is concluded to originate from production.

2.2 Determination of aniline in chalk

The 14 different products were analysed according to the standard EN 71-7 with minor necessary alterations described in the following paragraphs. Initially, analysis was performed including the reductive cleavage step to establish the total content of released aniline. Subsequently, 3 products with high content of aniline were selected in order to evaluate whether the aniline originates from the production process or azo colorants.

2.2.1 Method of analysis

The standard EN71-7 is intended for finger paint, and since the texture of chalk is different from finger paint, the sample preparation requires destruction of the chalk. Subsequently, 1 g of the test material could then be taken for analysis.

For the detection of aniline, the sample was treated with sodium dithionite in a citrate buffer (pH 6) at 70°C in a sealed vessel. It was observed that complete decolouration of the chalk did not occur during this treatment. Upon reductive cleavage, the resulting amines are extracted with MTBE by means of a SPE column. The ether extract was carefully concentrated and the residue was diluted in MTBE containing an internal standard. Subsequently, determination of aniline was performed by capillary gas chromatography with mass selective detector (GC-MS). For determination of free aniline, the reductive cleavage step was omitted. As a precaution, aniline-d5 was used as internal standard for quantification of aniline.

According to the standard EN71-7 aniline is together with other primary amines deemed to be determinable at levels exceeding 5 mg/kg. A recovery test was performed consisting of spiking of one of the test products with a known quantity of aniline. The results indicate that a content of aniline down to 1 mg/kg can be determined if released from the chalk.

The calibration of the analytical system used for determination of aniline facilitates determination of aniline at a concentration above 0.5 mg/kg.

2.3 Results

True determinations were performed twice for each product that was tested. The results stated in the table below are the average of the two determinations.

Analysis uncertainty: 0.6 - 21.7% RSD for determination of total content of aniline
0.5 - 16% RSD for determination of free aniline

TABLE 1. Content of aniline determined in 14 different products

Sample number	Total content of aniline [mg/kg]	Content of free aniline [mg/kg]
1	4.25	0.32*
2	4.33	0.30*
3	2.96	-
4	n.d.	-
5	4.12	-
6	2.43	-
7	2.45	-
8	3.37	-
9	3.79	0.30*
10	2.71	-
11	1.95	-
12	n.d.	-
13	4.92	-
14	2.26	-

- Means not determined

n.d. means not detected

* Results below the calibration range

For product no. 4 and product no.12 aniline could not be detected.

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