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of Chemical Substances
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Dichloromethane and 1,1,1-Trichloroethane in Hair-care Products

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CONTENTS

1. SUMMARY

The contents of dichloromethane, 1,1,1-trichloroethane (1,1,1-T) and other chlorinated solvents in cosmetic products are regulated by the Danish regulative on cosmetic products as well as by the Danish regulative on solvents and propellants in aerosol cans. 82 haircare products from the Danish market were analysed for the content of chlorinated solvents. One product was found to contain 472 ppm dichloromethane and 21 products (26%) were shown to contain traces to 89 ppm of dichloromethane/trichloromethane/tetrachloromethane/1,1,1-T/trichloroethylene/tetrachloroethylene. All of the above mentioned 22 products were in agreement with the Danish regulatives.

It is suggested that such a low content of chlorinated solvents in haircare products may be due to, 1) chlorinated solvents were used as carrier solvent, or 2) the respective products were contaminated with chlorinated solvents during their production. Thus, it seems that chlorinated solvents are not used as an active ingradient in haircare products.

2. INTRODUCTION

Dichloromethane, 1,1,1-trichloroethane (1,1,1-T) and other chlorinated organic solvents are toxic to human health (1-3). It has been demonstrated that groundwater at many places around the world is contaminated with chlorinated organic solvents (4-8). Recently, it has been shown that some of the chlorinated solvents, like the fully halogenated chlorofluorocarbons (CFC), can deplet the ozone layer in the statosphere (9). Thus, compared to ozone layer depleting potential of CFC-11 as 1, the ozone layer depleting potential of 1,1,1-T and tetrachloromethane has been found to be 0.13 and 1.1 respectively (9). In the second meeting of the members of Montreal Protocol, it has been adopted that the member countries will reduce the consumption of 1,1,1-T, besides many other CFC's and tetrachloromethane (10). The reduction will be 100% by the year 2005.

Dichloromethane and 1,1,1-T should not be used in cosmetic aerosol products according to a Danish regulative on solvents and propellant in aerosol cans. This is also prohibited by the Danish regulative on cosmetic products. However, according to the cosmetic regulative, up to 35% of dichloromethane and/or 1,1,1-T may be used in non-aerosol cosmetic products. Other chlorinated organic solvents, tri- and tetrachloromethane as well as tri- and tetrachloroethylene must not be used in cosmetic products, according to the cosmetic regulative.

In the present work, haircare products form the Danish market have been investigated for the content of dichloromethane, 1,1,1-T and other chlorinated organic solvents.

3. SAMPLES

Haircare products, hair spray, hair mousse, hair wax, hair gel, and so on, were collected from the Danish retail market as well as from the Danish manufactrures/importers, in the period January to April 1990. The samples collected were both aerosol and non-aerosol products, and they represented products both for professional and private use. A total of 82 products from 27 companies were investigated (Table 1).

Table 1: Haircare products investigated.

Sample No.	Sample identification	Manufacturing Co./ distributor
040	Exclusive hair spray, extra hold	Nordisk Parfumevarefabrik, Denmark.
041	Royal d'or hair spray, crystal clear	Nordisk Parfumevarefabrik, Denmark
042	Exclusive hair mousse	Nordisk Parfumevarefabrik, Denmark
043	DKS form mousse with silk protein	Dansk Kosmetik Salg A/S, Denmark
044	Sainsbury's hair spray, extra hold	J. Sainsbury's plc., UK
045	Streetwise style and fix spray, mega hold	Manhattan Style Academy Ltd., UK
046	Energance form foam, without alcohol	L'oreal, France
047	Bellady color mousse	Wella, Germany
048	Free style form foam, extra strong hold	L'oreal, France

Table 1.: Continued.

Sample No.	Sample identification	Manufacturing Co./distributor
049	Happy hair frisure gelé spray, normal hold	Dansk Kosmetik Salg A/S, Denmark
050	Streetwise styling mousse, mega hold	Manhattan Style Acaemy Ltd, UK
051	Studo line foam gelé, extra hold	L'oreal, France
052	Helen Curtis Spraynet hair spray, Crystal clean	Barnängen A/S, Denmark
053	Alberto normal form foam	Mölnlycke, Sweden
054	Helen Curtis Lanolin spray, hair conditioner	Barnängen A/S, Denmark
055	Studio line fix spray, normal hold	L'oreal, France
056	Elnett Satin, extra strong fixer	L'oreal, France
057	Happy Hair, hair spray, extra hold	Dansk Kosmetik Salg A/S, Denmark
058	Elect Colorset, Silver	L'oreal, France
059	Nana hair gelé	We-Ha Kosmetik, Denmark
060	Happy Hair form cream	Dansk Kosmetik Salg A/S, Denmark
061	DKS hair wax	Dansk kosmetik Salg A/S, Denmark
062	Studio line form cream	L'oreal, France
063	Studio line shining wax	L'oreal, France
064	Swiss haircare, conditioner with dex panthenol	Laboratories St. Ives S.A., Switzerland
241	LANCOS sober styling mousse, normal	Landskrona Cosmetics, Sweden
242	Breck hair spray, normal hold	Shulton b.v., Netherlands
243	Gunnar's style mousse	E. J. Production, Denmark
244	Tina hair spray	Magasin du Nord, Denmark

Table 1.: Continued.

Sample No.	Sample identification	Manutacturing Co./ distributor
245	Stuhr Careline hair spray	E.S. Production, Denmark
246	Nana hair gelé spray	We-Ha Kosmetik, Denmark
247	Nana luxury hair spray	We-Ha Kosmetik, Denmark
248	Nana hair form cream	We-Ha Kosmetik, Denmark
249	Jane Hellen volym mist hair spray	Pierre Robert, Sweden
251	Flex styling mousse	Revlon, U.S.A
252	Naturelle hair mousse	Pierre Robert, Sweden
253	Naturelle volym spray mist	Pierre Robert, Sweden
254	Naturelle hair spray, silky formula	Pierre Robert, Sweden
255	Hair Styling mousse	Catzy, Sweden
256	Breck styling mousse form foam, extra style	Shulton b.v., Netherlands
382	Sharpers hair spray, normal hold	Oriflame, U.K.
383	Sharpers styling mousse	Oriflame, U.K.
384	Wellin mousse form foam	Wella, Germany
385	Helena Hector's hair mousse	Nord Tend, Denmark
386	Hair mousse form foam	FDB, Denmark
387	Brugsen hair spray	FDB, Denmark
388	Shea mousse	Bella Vista A/S, Denmark
389	Tribella hair spray, ultra strong	Bella Vista A/S, Denmark
390	Strukture mousse	Bella Vista A/S, Denmark
391	Bell mousse	Bella Vista A/S, Denmark
421	Hair mousse	Irma A/S, Denmark
422	Hair spray	Irma A/S, Denmark
423	Hair lacquer spray	Matas A/S, Denmark
424	Hair gelé, strong	Matas A/S, Denmark
425	Form foam	Matas A/S, Denmark

Table 1.: Continued.

Sample No.	Sample identification	Manufacturing Co./ distributor
426	Form foam with silk protein	Matas A/S, Denmark
427	Form foam, extra hold	Matas A/S, Denmark
428	Gelé spray	Matas A/S, Denmark
429	Hair lacquer	Matas A/S, Denmark
432	Hair spray, easy to brush off	Nordiske Parfumevarefabrik, Denmark
433	Sound fix spray	Trendy, Germany
434	Hairlife light hair spray, only for salon use	Imperial Kosmetik A/S, Denmark
435	Hairlife light mousse super	Imperial Kosmetik A/S, Denmark
436	Hairlife light hair shine	Hans Schwarzkopf GmbH, Germay
437	Novelle form mousse	Hans Schwarzkopf GmbH, Germany
438	Natural styling mousse, apre's styling	Hans Schwarzkopf GmbH, Germany
439	Natural styling mousse, strong hold	Hans Schwarzkopf GmbH, Germany
440	Natural styling hair spray	Hans Schwarzkopf GmbH, Germany
441	Young Style forming spray, ultra strong	Hans Schwarzkopf GmbH, Germany
450	System Professional styling foam	Wella, Germany
458	Wellin gelé spray, extra hair volume	Wella, Germany
461	High Hair foam, extra strong	Wella, Germany
462	Wellin hair gelé, extra strong	Wella, Germany
463	System Professional styling gel	Wella, Germany
464	High Hair gelé, extra strong	Wella, Germany

Table 1.: Continued.

Sample No.	Sample identification	Manufacturing Co./ distributor
465	High Hair wax	Wella, Germany
466	System Professional lacquer	Wella, Germany
467	Form & Fülle hair spray with bambus extract	Wella, Germany
468	Wellin hair spray, normal hold	Wella, Germany
469	High Hair gelé spray	Wella, Germany
470	System Professional hair spray	Wella, Germany

4. Methods.

Dichloromethane, 1,1,1-T and other chlorinated solvents in the haircare products were determined by a headspace gas chromatographic (GC) method. Headspace vials and teflon coated silicone septa for the vials were preheated at 150°C for 16 hours before use. The samples for the headspace analysis were prepared as follows:

4.1 Sample Preparation.

4.1.1 Non-aerosol Products.

The products were homogenized, by shaking, stirring or blending, before subsampling. Approximately 50 mg (50 µl) of a sample was weighed accurately in a 10 ml headspace vial, and that was closed with a teflon coated silicone septum, immediately after weighing. For each sample at least 4 vials were prepared simultaneously.

4.1.2 Aerosol Products (except foam products).

An aerosol can containing a haircare product was weighed, and then it was frozen for approximately 5 min in liquid nitrogen. The frozen can was punctured and that was allowed to stand in a fume cupboard at room temperature (20°C). When the contents in the aerosol can had melted and the propellant was evaporated (temperature of the aerosol can 15°C approximately), it was weighed again. The content in the aerosol can (analyte) was transferred into a brown glas bottle, which was then closed tightly with a screw cap. The empty aerosol can was weighed. The net weight of the product "x", (weight of the aerosol can with product - weight of the empty aerosol can), and the weight of the analyte "y" (weight of the punctered aerosol can without propellant - weight of the empty aerosol can) were calculated. Immediately after transferring the analytes into brown bottles, they were subsampled for headspace analysis as described for the non-aerosol products. The analytes were stored at 4°C.

4.1.3 Hair Mousse in Aerosol Cans (foam products).

An aerosol can containing hair mousse was weighed and shaked well before subsampling. A portion of the sample was transferred (by pressing the nozzle of the aerosol can) into a 20 ml headspace vial, so that approximately half of the vial was filled with the foam. Care should be taken to avoid any loss of the expelled material from can, all of it must be transferred into the vial. The vial was then closed immediately with a teflon coated silicone septum. The aerosol can was weighed again. The amount of sample in the headspace vial = difference between the weight of the aerosol can before

and after subsampling.

4.2 Headspace GC Analysis.

The samples in the headspace vials were analysed using a Hewlett Packard (HP) gas chromatograph coupled with a HP 19395A headspace autosampler and a HP 3393A integrator, as follows:

4.2.1 Headspace Autosampler.

Oil-bath temperature:	80°C.
Loop temperature:	130°C.
Loop volume:	1 ml.
Carrier gas:	N_2, flow 20 ml/min.
Injection time:	3 min.

4.2.2 Gas Chromatograph.

GC column:	Chrompack CP-sil-5 CB, 60 m x 0.32 mm (i.d), df 1.2 µm.
Temperature program:	3 min at 40°C, thereafter 5°C/min to 250°C, 0.5 min at 250°C.
Carrier gas:	N_2, flow 30 ml/min.
Injector:	Splitter, split 1:50, 250°C.
Detector:	ECD, 280°C.
Make-up gas:	N_2, 50 ml/min.

4.3 Reproduction, Calibration Curves and Quantitation.

Two samples were analysed 10 times to calculate relative standard deviation (R.S.D.) of the method. External standard method was used for the quantitation of the solvents in the samples. GC peak areas were used for the quantitation of solvents. 50 µl of 0-1% of all the solvent standards, diluted in isopropanol, were analysed under the same conditions as the samp-

les. Calibration curves for the amount of solvent versus GC peak area were prepared. All the samples as well as standards were analysed in duplicate.

4.4 Calculation.

The amount "m_1" (g) of a solvent corresponding to its GC peak area was read on the respective calibrations curve. The concentration (C) of the solvent in the sample was calculated as follows:

For non-aerosol products (4.1.1) and foam products in aerosol cans (4.1.3):

$$\%C = \frac{m_1}{m} 100$$

where m is the amount (g) of the sample analysed.

For aerosol products (4.1.2):

$$\%C = \frac{m_1}{m} 100 \frac{y}{x}$$

where x is the net weight (g) of the product in the aerosol can, and y is the weight (g) of analyte (weight of the product - weight of the propellant) in the aerosol can.

Solvent concentrations in the samples were expressed in ppm, by multiplying % C with 10^4.

Table 2.: The contents of dichloromethane and 1,1,1-T in the samples investigated.

Sample No.	Content in ppm	
	Dichloromethane	1,1,1-T
044	89	-
051	-	13
056	472	-
440	43	-

Besides above mentioned, one of the investigated sample was shown to contain 3 ppm tetrachloromethane and 4 other samples contained 5-20 ppm tetrachloroethylene (Table 3). Furthermore, traces of chlorinated solvents (close to detection limits) were identified in a number of samples (Table 4). The solvents in these samples were not qunatitated. Some examples of GC chromatograms of chlorinated solvent - containing haircare products are shown in Figures 1-5.

Table 3.: The content of other chlorinated solvents in the samples investigated.

Sample No.	Solvent	Content in ppm
241	Tetrachloroethylene	5
250	Tetrachloromethane	3
256	Tetrachloroethylene	13
439	Tetrachloroethylene	16
460	Tetrachloroethylene	20

Table 4.: Haircare products which contained traces of chlorinated organic solvents.

Sample No.	Solvents identified
040	Tetrachloroethylen
045	Dichloromethane
048	Trichloromethane
050	Trichloromethane, trichloroethylene
056	Trichloro- and tetrachloroethylene
057	Trichloromethane
243	Dichloromethane
250	Trichloromethane
251	Trichloromethane
421	1,1,1-T
422	1,1,1-T, tetrachloroethylene
432	1,1,1-T
435	Tetrachloroethylene
438	Tetrachloroethylene
439	Trichloromethane
469	Dichloromethane

One of the haircare products (sample no. 056) analysed in the present study was shown to contain significant amount of 1,1,1,-T (approximately 0.05%). 21 of the remaining products (26%) were found to contain traces to 0.01% of chlorinated solvents. The results of the present study may thus indicate that the chlorinated solvents were not used as an active ingradient in these products. It is possible that the chlorinated solvents were used as "carrier solvent" in the above mentioned haircare products. However, it can not be ruled out that the small amounts of chlorinated solvents found in 26% of the hair products may be due to a contamaniation of these products during the productions.

5. Results and Discussion.

Chlorinated solvents in the present investigation have been identified by comparing their GC retention times (t_R) with t_R of solvent standards. The detection limits of the solvents analysed were as follows: dichloromethane 10 ppm, 1,1,1-T 2 ppm, trichloromethane 1 ppm, tetrachloromethane 0.2 ppm, trichloroethylene 0.5 ppm and tetrachloroethylene 0.2 ppm. The calibration curves of all the standard solvents were linear in the concentration range 0-1%. The R.-S.D. of the method of quantitation was found to be < ± 3% for all the solvents. The external standard method used for the quantitation of solvent in the present study does not take account of the sample matrix.

Three of the investigated products were found to contain 1,1,1-T and one product contained dichloromethane (Table 2). The concentrations of dichloromethane/1,1,1-T in all the 4 products were < 500 ppm (0.05%). All of the 4 products were in agreement with the Danish aerosol regulative which regulates contents of solvents (only in concentrations > 1%) in aerosol cans. As the cosmetic regulative allows up to 35% of dichloromethane and/or 1,1,1-T in non-aerosol cosmetics, the above mentioned 4 samples were also in agreement in with the cosmetic regulative.

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Figure 1: Gas chromatogram of isopropanol (blank).

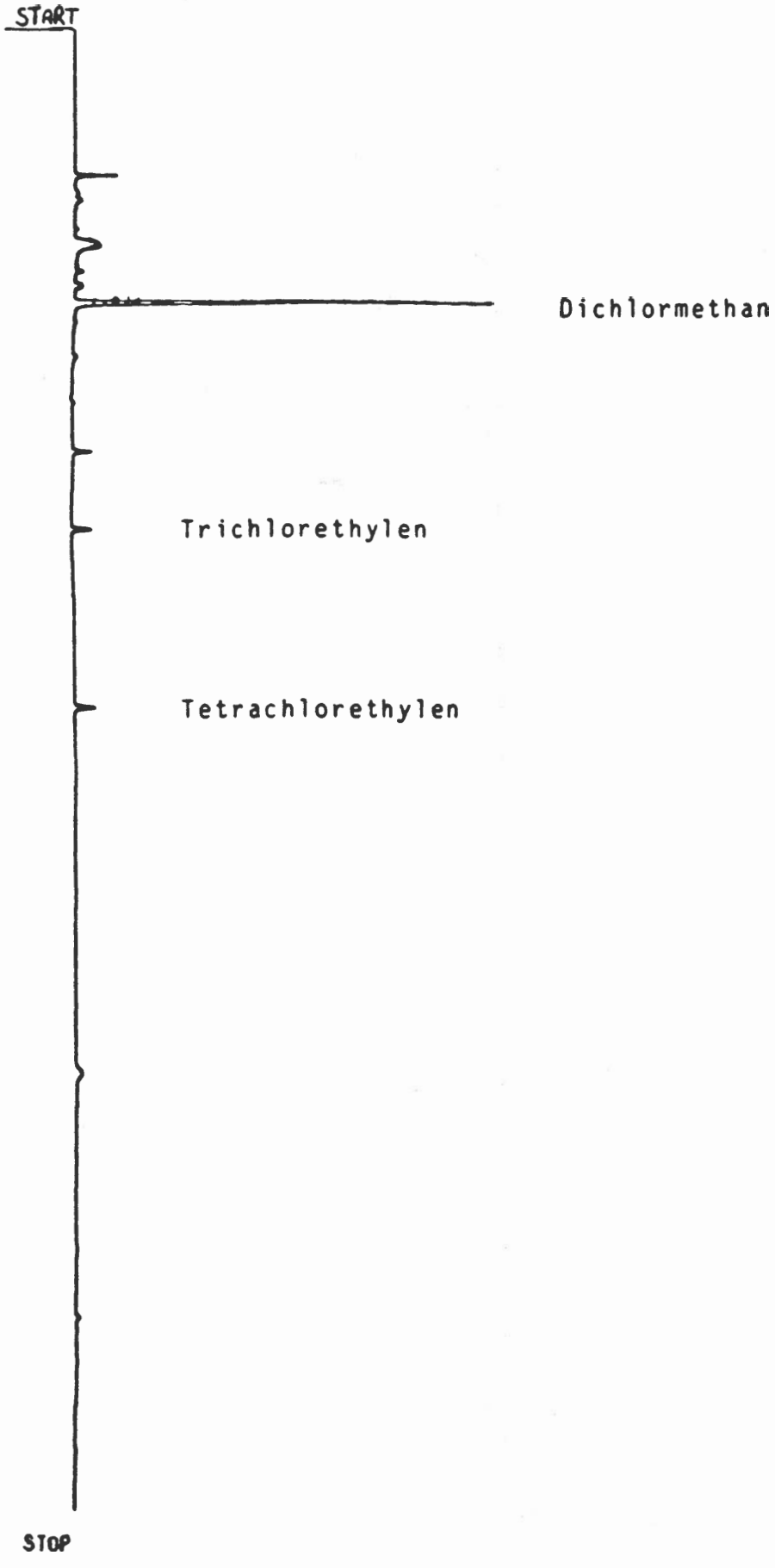

Figure 2: Gas chromatogram of sample no. 56.

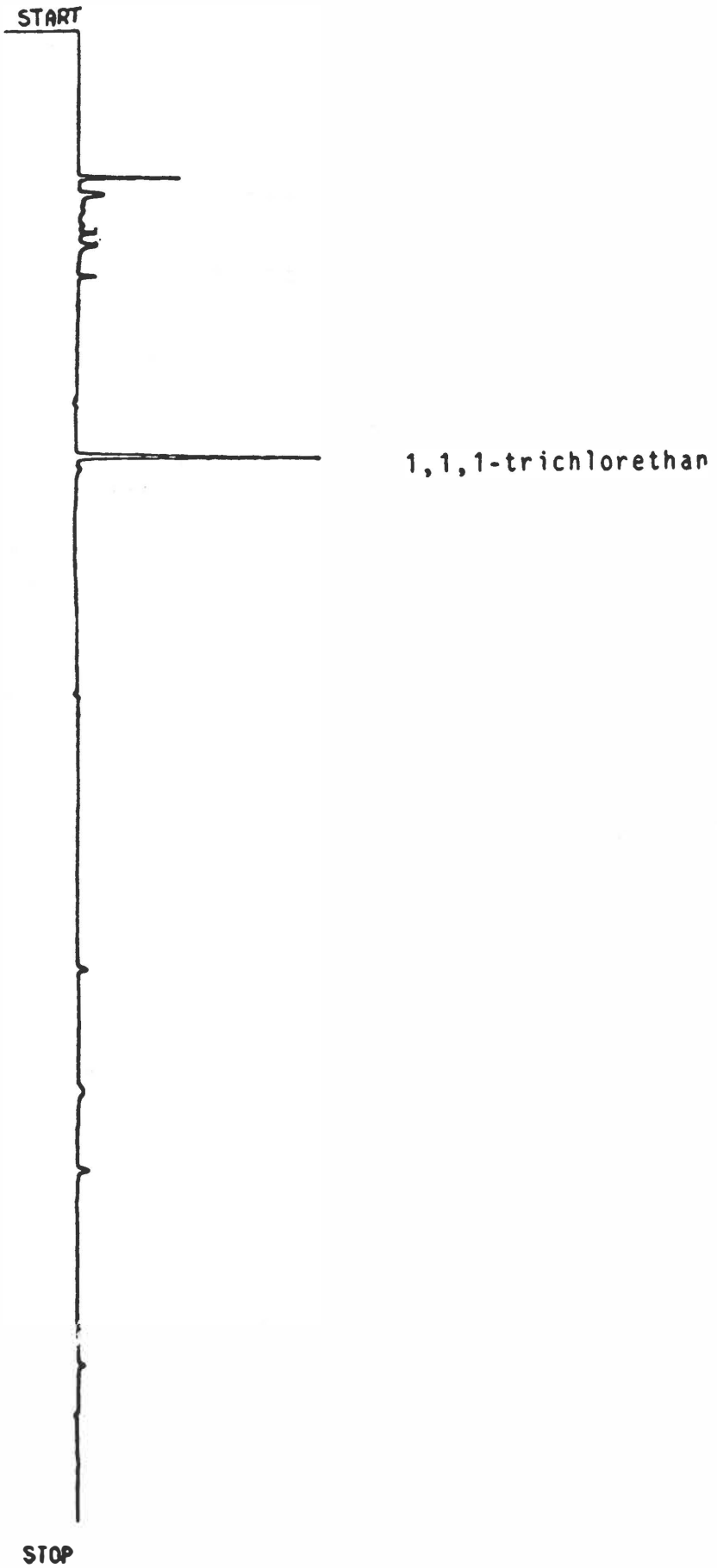

Figure 3: Gas chromatogram of sample no. 51.

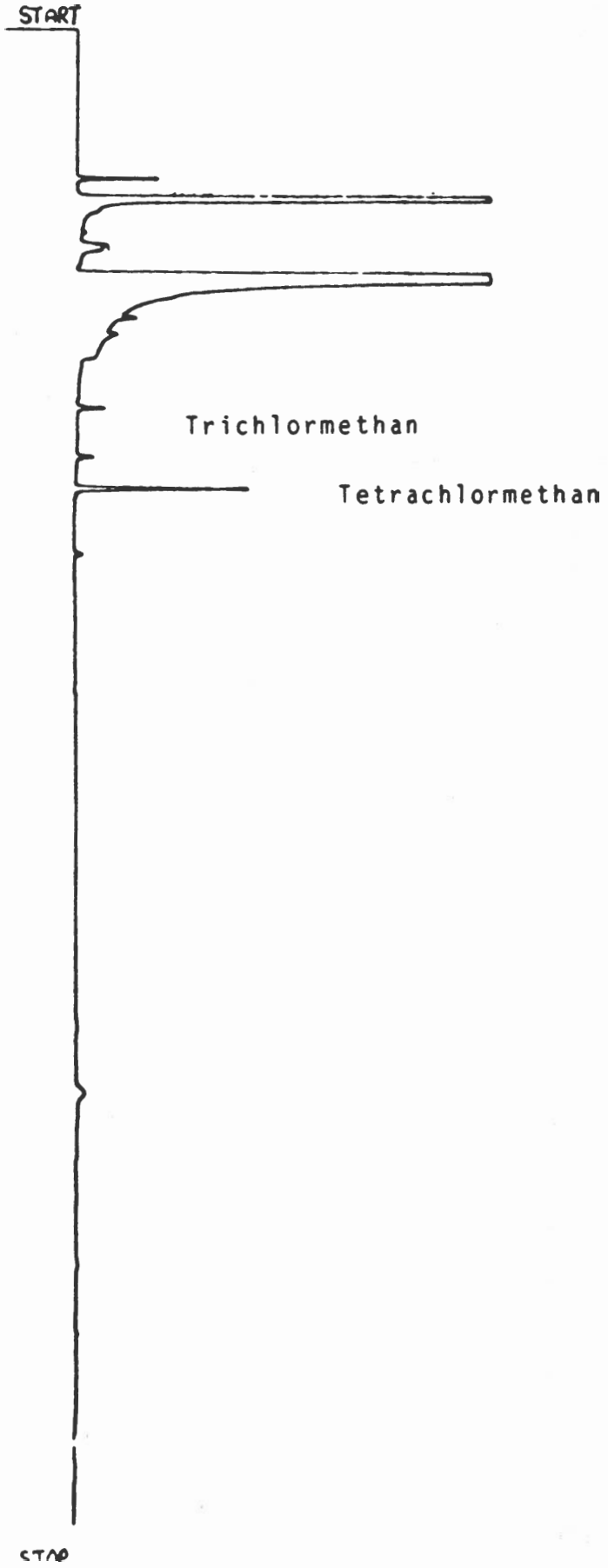

Figure 4: Gas chromatogram of sample no. 250.

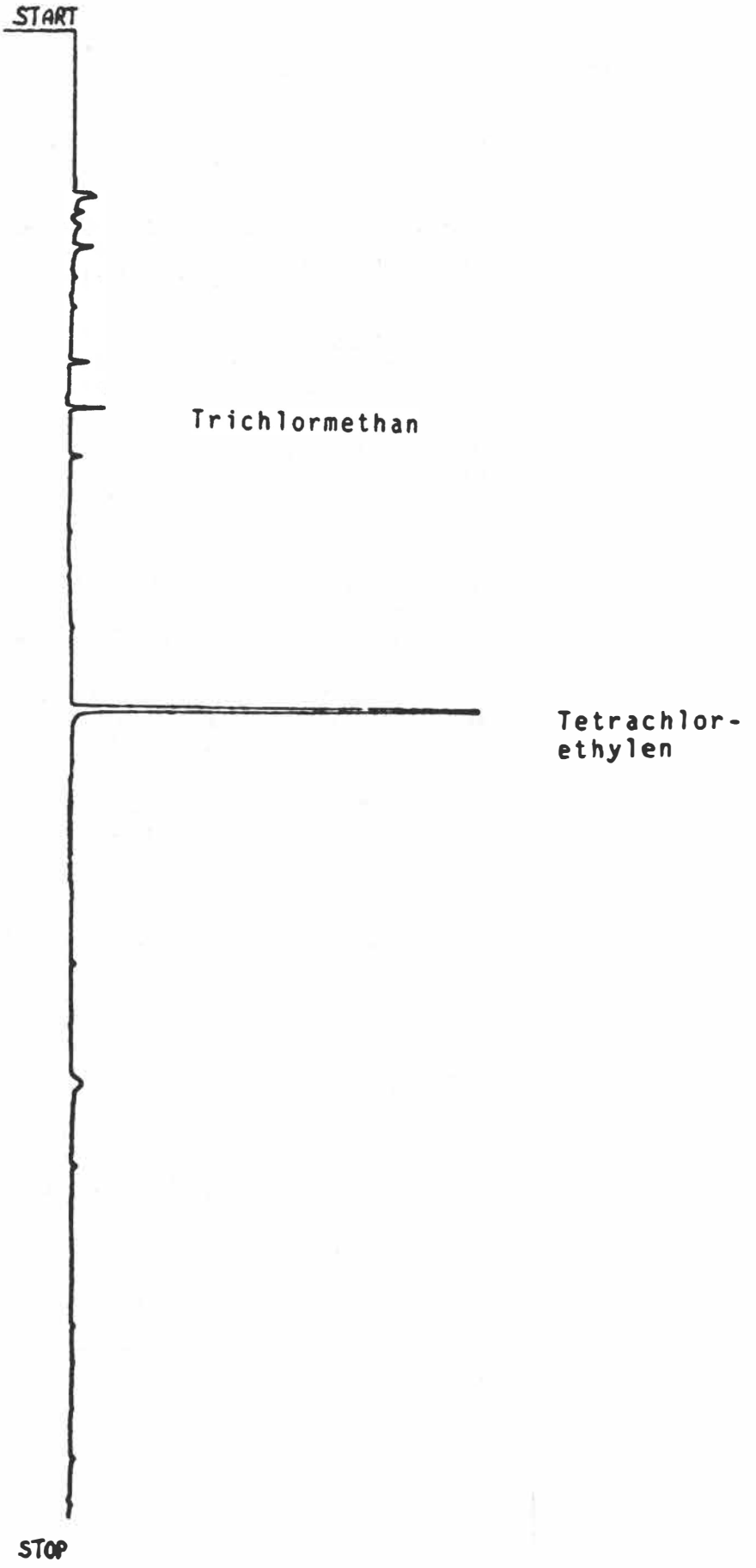

Figure 5: Gas chromatogram of sample no. 439.

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