Hydrogen Sulfide and Acetaldehyde Discharge from a Rapeseed Extraction Plant[1]

L.A. Lindh and **J.Å.H. Dahlén**
Svensk Oljeextraktion AB, P.O. Box 3, S-374 21 Karlshamn, Sweden

The gas effluent from a mineral oil recovery system in a rapeseed extraction plant contains high concentrations of hydrogen sulfide and acetaldehyde. The two compounds are produced in the desolventizer-toaster (DT) and are the major cause of the unpleasant smell emanating from the plant.

Most rapeseed extraction plants are provided with a mineral oil recovery system to reduce the emission of hexane. The gas effluent from the system has an unpleasant smell and pollutes the environment. Reports have been published indicating that the processing of rapeseed and rapeseed products produces hydrogen sulfide, methyl mercaptan, dimethyl sulfide, carbon disulfide and acetaldehyde (1,2).

An investigation was made in an existing extraction plant to determine the main components in the gas effluent from the mineral oil recovery system. During the test period, the average flow of waste gases amounted to 100 m^3/hr (22°C). The hexane content was 10,000–20,000 mg/m^3 according to a hexane calibrated TLV sniffer (Bacharach Instrument Co.). The average rapeseed processing capacity was 850 tons/24 hr. The calculated retention time in the DT was 40 min. Between 2,000 and 2,400 kg/hr of live steam was injected. The moisture content in desolventized meal was 14.5–16.5%.

The analyses were made by gas chromatography (GC) with olfactometric detection, flame ionization detector (FID), flame photometric detector (FPD) and mass spectrometer (MS). HPLC analyses were made on hydrazone derivatives.

The analyses showed that hydrogen sulfide and acetaldehyde were the main contributers to the unpleasant smell. Experiments were made in order to find the sources of hydrogen sulfide and acetaldehyde.

EXPERIMENTAL

Gas chromatography with olfactometric detection. The GC was a dual Varian 3700 equipped with two FIDs. One channel was provided with a 1.8-m × 2.0-mm i.d. stainless steel column packed with 60/80 Carbopack C/0.2% Carbowax 1500. The temperature of the injector was 200°C and of the column 30°C. The FID was kept cool and provided with a teflon tube on the flame tip leading to the nose of the analyst. 1.0 ml of gas from the effluent was injected.

Gas chromatography with FPD (3). The GC was a HP 5880 A with a flame photometric detector (FPD 100 AT, Meloy Lab. Inc.) operated at 200°C. A chromosil 330, 2.5-m × 1/8" o.d. FEP teflon column packed with a modified silica gel specifically treated to separate carbonyl sulfide, hydrogen sulfide, carbon disulfide, C1–C3 mercaptans and alkylsulfides, was used. The temperature of the injector was 60°C. The column temperature program was 3 min at 1°C, 20°C/min up to 41°C, 16°C/min up to 100°C and held for 20 min. Ten ml/min of nitrogen was used as carrier gas + 40 ml/min as make up gas.

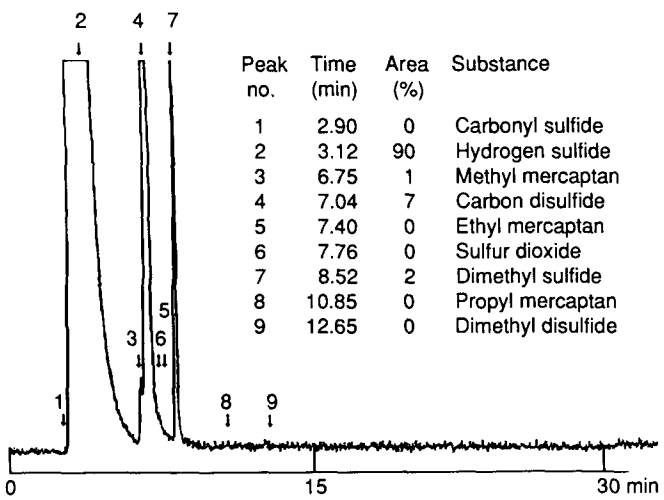
Aldehydes in air (4). Two hundred ml of the gas effluent from the mineral oil recovery system was sucked through a gas washing bottle with 80 ml solution of 5 mM 2,4-dinitrophenylhydrazine in 2 M HCl. The solution was extracted with 2 × 80 ml of isooctane. The isooctane phase was washed with 20 ml of water and extracted with 20 ml of acetonitrile. HPLC identification was made on a 20-cm 5 μ C18-column with UV detection at 254 nm. The mobile phase was 1.0 ml/min of acetonitrile/water (70/30) and 10 μl of the acetonitrile extract was injected.

Hydrogen sulfide in air. A Dräger tube marked "H_2S 0,2%/A" from Drägerwerk AG Lübeck, Germany, was inserted in the gas effluent from the mineral oil recovery system and a suitable number of strokes were made with the gas detector pump in order to get an accurate reading on the tube. A selective reaction with hydrogen sulfide and mercaptans was indicated.

Standardization. Acetaldehyde (0.1% pure) in water was used as standard in the GC and HPLC analyses.

RESULTS AND DISCUSSION

The first analysis of gas effluent was made on an activated carbon column with olfactometric detection. Hydrogen sulfide and acetaldehyde could be recognized from their very characteristic smells. No other compounds could be detected by this method. Further analyses with GC-MS confirmed the results and also showed small amounts of carbon disulfide and dimethyl sulfide. GC analysis with FPD (Fig. 1) showed, in addition, small amounts of methyl mercaptan.



Peak no.	Time (min)	Area (%)	Substance
1	2.90	0	Carbonyl sulfide
2	3.12	90	Hydrogen sulfide
3	6.75	1	Methyl mercaptan
4	7.04	7	Carbon disulfide
5	7.40	0	Ethyl mercaptan
6	7.76	0	Sulfur dioxide
7	8.52	2	Dimethyl sulfide
8	10.85	0	Propyl mercaptan
9	12.65	0	Dimethyl disulfide

FIG. 1. Gas chromatographic analysis with flame photometric detector of gas effluent. Expected positions for peaks 1, 5, 6, 8 and 9 (not detected) were determined by separate injections of the corresponding compounds.

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The conclusion from these findings was that it was possible to determine the content of hydrogen sulfide using Dräger tubes, without interference from other compounds.

Aldehydes were analyzed as the corresponding hydrazone derivatives. Gas from the effluent was sucked through 2,4-dinitrophenylhydrazine solution and analyzed by HPLC. One dominating peak was found and identified as acetaldehyde (Fig. 2).

Results from quantitative analyses performed in 1987 and 1988 are shown in Table 1.

The low content of glucosinolates in the double low meal as compared to single low meal does not result in a corresponding decrease in hydrogen sulfide production (Table 1). This indicats that other sulfur-containing compounds may be partly responsible for the release of hydrogen sulfide (1).

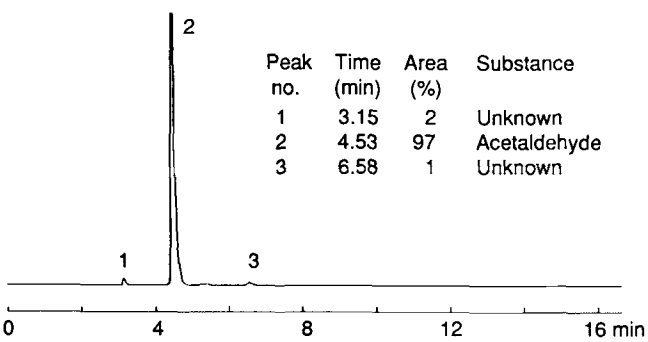

FIG. 2. High performance liquid chromatographic analysis on hydrazone derivatives.

TABLE 1

Hydrogen Sulfide and Acetaldehyde Content in Gas Effluent from a Mineral Oil Recovery System When Processing Single and Double Low Rapeseed

Seed type	Glucosinolates[a] (μmol/g ddm[b])	Hydrogen sulfide		Acetaldehyde	
		Number[c]	g/m³	Number[c]	g/m³
Single low	62	24	9.5	7	8.2
Double low	18	9	6.1	2	6.7

[a] Mean value in meal over the period.

[b] Ddm, defatted dry matter.

[c] Number of analyses.

TABLE 2

Release of Hydrogen Sulfide from 1.0 g Each of Cystine, Cysteine and Sinigrin (Reference), Respectively, Under DT Conditions

	Mol wt	Test sample 1.0 g (mmol)	Hydrogen sulfide in gas phase (mmol)
Cystine	240	4.1	0.000
Cysteine	121	8.3	0.026
Sinigrin	397	2.4	0.012

TABLE 3

Release of Acetaldehyde from 1 kg of Rapeseed in an Air Current (2.5 l/hr) at Different Temperatures

Seed type	Seed age (months)	Seed temp (°C)	Time (hr)	Acetaldehyde (mg/kg of seed)
Double low	10	20	91	0.05
Double low	10	50	20	2.56
Double low	10	90	20	20.10

In attempts to find additional sources of hydrogen sulfide, 1.0 g each of cystine, cysteine and sinigrin (ref.), respectively, was enclosed in a 60-ml head-space bottle together with 0.18 g (15%) water. To imitate the processing conditions in a DT, the bottle was kept for 1 hr in an oven at 100°C. The gas phase (head space) was analyzed using Dräger tubes. The results are shown in Table 2.

It is well know that DT gases, rich in hydrogen sulfide, are strongly corrosive. As hydrogen sulfide dissolves in circulating hexane and in steam condensate, it is also to a great extent responsible for the corrosive atmosphere throughout the rapeseed extraction plant (5).

The authors have no explanation for the presence of acetaldehyde in the waste gases. It was shown, however, that if an air current is forced through a bed of whole rapeseeds, it takes up a certain amount of acetaldehyde. Results from tests with double low seed at different temperatures are shown in Table 3.

The amount of acetaldehyde released at 90°C corresponds to what was found in the waste gases from the plant.

Samples of single low seed, newly harvested and stored for one and three months, respectively, also developed acetaldehyde. The amount varied in an unpredictable way and was at least 0.52 mg/kg of seed at 20°C in one test.

Because aldehydes are toxic to living matter (6), it is tempting to speculate whether it may be part of a defense system to protect the seed against microorganisms.

It should be noted that the presence of acetaldehyde influences the quantitative determination of hexane by the TLV sniffer. Up to 40% of the "hexane" value could, in reality, be acetaldehyde.

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