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IDENTIFICATION OF VOLATILES IN THE HEAD SPACE OF ACID-TREATED PHOSPHATE ROCK BY GAS CHROMATOGRAPHY–MASS SPECTROMETRY

H. VAN LANGENHOVE* and N. SCHAMP

Laboratory of Organic Chemistry, Faculty of Agricultural Sciences, State University of Gent, Coupure links 653, B-9000 Gent (Belgium)

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SUMMARY

Phosphate rock samples were treated with sulphuric and hydrochloric acid. Compounds volatilized during this treatment were sampled on Tenax GC and analysed by gas chromatography–mass spectrometry. The identification revealed the presence of a few organosilicon fluorides, as well as numerous hydrocarbons and organosulphur compounds. A mercaptan, acyclic and cyclic sulphides, disulphides and alkylthiophenes were fully or partially identified. Since the human olfactory system is about 1000 times more sensitive for sulphur compounds than for hydrocarbons, it was concluded that the sulphur compounds were responsible for the typical pungent odour of the headspace mixture.

INTRODUCTION

The current annual consumption of phosphate rock, as the raw material for phosphorus chemicals and fertilizers is about 130 million tonnes. The major part of this commercial phosphate rock is mined from ores of marine sediments, in which phosphate occurs as carbonate-apatite¹.

About 90% of all phosphate rock is processed by the “wet process”, which essentially is a treatment of the rock with a mineral acid. Sulphuric acid is generally used, but depending on the desired end-products, phosphoric, hydrochloric or nitric acid are used as well. In order to minimize the environmental impact of the wet process, some control measures have to be taken. When sulphuric acid is used, *ca.* 5–6 tons of phosphogypsum are produced per ton of phosphorus pentoxide. Since this gypsum is impure, it is not competitive with mined gypsum for the building industry and therefore it has to be disposed of. Besides, phosphate rock contains between 2.5 and 4.5% of fluorine. Much of this fluorine is volatilized as hydrogen fluoride and silicon tetrafluoride during acid treatment. To prevent the release of these compounds into the environment gases are scrubbed with water.

Another problem is the characteristic sour odour which is observed in the neighbourhood of phosphate plants, and which may sometimes constitute a public

nuisance. The compounds responsible for the odour have yet not been identified. Therefore phosphate rock samples were treated in the laboratory with mineral acids; head-space volatiles were concentrated by adsorption on Tenax GC and the volatiles present in the head-space samples were identified by gas chromatography–mass spectrometry (GC–MS).

EXPERIMENTAL

Adsorption sampling

Before adsorption tubes were packed with Tenax GC, the adsorbent was extracted for 24 h with acetone, in a Soxhlet apparatus, and dried by evaporating the solvent under reduced pressure. Glass tubes (15 × 0.8 cm I.D.) were filled with 0.75 g of adsorbent, which was positioned between two glasswool plugs. Before use, packed tubes were conditioned by heating (220°C) overnight under a helium flow.

Fig. 1 illustrates the sampling apparatus. Samples were placed in a three-necked flask, which was mounted in a waterbath to keep the temperature at 60°C. Acid was added through a separatory funnel, and a helium supply was connected. In the initial stage of acid treatment, gas evolved spontaneously from the phosphate rock. After that a helium flow of 0.2 l/min was started in order to transfer head-space volatiles to the adsorption tube. Gas volumes were measured with a wet-gas meter.

The phosphate rock used in these investigations originated from Morocco. It consisted mainly of small pellets of marine origin. In the experiments 20 g of phosphate rock were treated with 100 ml of acid and 5 l of gas were sampled.

GC–MS analyses

A laboratory-made thermal desorption system² was used to concentrate adsorbed volatiles before GC–MS analyses. The GC–MS apparatus consisted of a Varian 2700 gas chromatograph fitted with a flame ionization detector, and a MAT 112 mass spectrometer.

A glass column (100 m × 0.5 mm I.D.) statically coated with SE52 (2 mg/ml) was used. Temperature programmes were varied from one analysis to another. The usual detector sensitivity was 80 pA/mV. Mass spectrometer conditions were as follows: source pressure, 10⁻⁶ Torr; electron energy, 70 eV; emission current, 0.7 mA; scan range, 0–250 *m/e*; scan speed, 100 mass units/s. Mass spectrometer scans were performed according to the signal from the flame ionization detector.

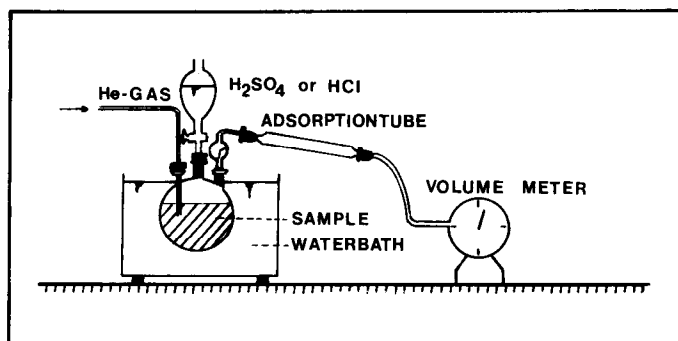


Fig. 1. Schematic drawing of the sampling apparatus.

Synthesis of reference compounds

In order to confirm results of the interpretation of mass spectra, some reference compounds were synthesized. To synthesize 2-methyl thiacyclohexane, 2-methylpiperidine was benzoylated and the N-benzoylpiperidine was treated with phosphorus pentabromide to obtain 2,6-dibromohexane. The substitution and cyclization with sodium sulphide was carried out according to the procedure of Whitehead *et al.*³. The purity of the compound was checked with GC and flame photometric detection (FPD) and it was necessary to perform preparative GC (Carbowax 20M 10% on Chromosorb W/AW, 3 m × 3 mm I.D.) with catharometer detection, to obtain the pure compound.

Disulphides were prepared by oxidation of mercaptans with iodine, according to McAllen *et al.*⁴. This reaction was carried out with methanethiol-ethanethiol; methanethiol-1-propanethiol and methanethiol-2-propanethiol. Since these compounds were used for the determination of Kovats indices and reference mass spectra by GC-MS, no effort was made to separate the three different disulphides present in each reaction mixture.

Asymmetric sulphides were prepared by nucleophilic substitution of a halogenide with a mercaptide⁵. This reaction was carried out with ethanethiol-iodomethane, methanethiol-2-bromopropane and propanethiol-iodomethane.

GC-FPD analyses

GC-FPD analyses were performed on a Tracor 560 instrument with a glass capillary column (50 m × 0.5 mm I.D.) statically coated with SE52 (2 mg/ml). This system was equipped with the same thermodesorption system as the GC-MS apparatus.

RESULTS

Blank analyses

It has been established that artefacts may be formed during adsorption sampling on porous polymers such as Tenax GC or XAD-2^{6,7}. In order to check the sampling procedure, the sampling flask was flushed with helium (0.5 l/min, 10 min). A conditioned adsorption tube was then connected, and 5 l of helium gas were sampled through the system. As can be seen from Fig. 2 no artefacts were detected under these conditions. This does not conflict with literature results because artefact formation occurs primarily during sampling at elevated temperatures (more than 100°C) and in oxidizing atmospheres. Besides, according to Hanson *et al.*⁶ the major degradation product of Tenax GC is 2,6-diphenylquinone, a high-boiling compound (M.W. 260) that will probably not desorb from Tenax GC under the conditions used in the present study (maximum desorption temperature 220°C).

Identification of volatiles in raw materials

In a first series of experiments, the volatiles present in the head space of raw materials were identified. These raw materials included: distilled water (100 ml); phosphate rock (20 g) and distilled water (100 ml); hydrochloric acid (50 ml, 36 N) and distilled water (100 ml). In each case 5 l of helium were used as transfer gas. Results of the GC-MS analyses of these samples are presented in Table I, and a typical

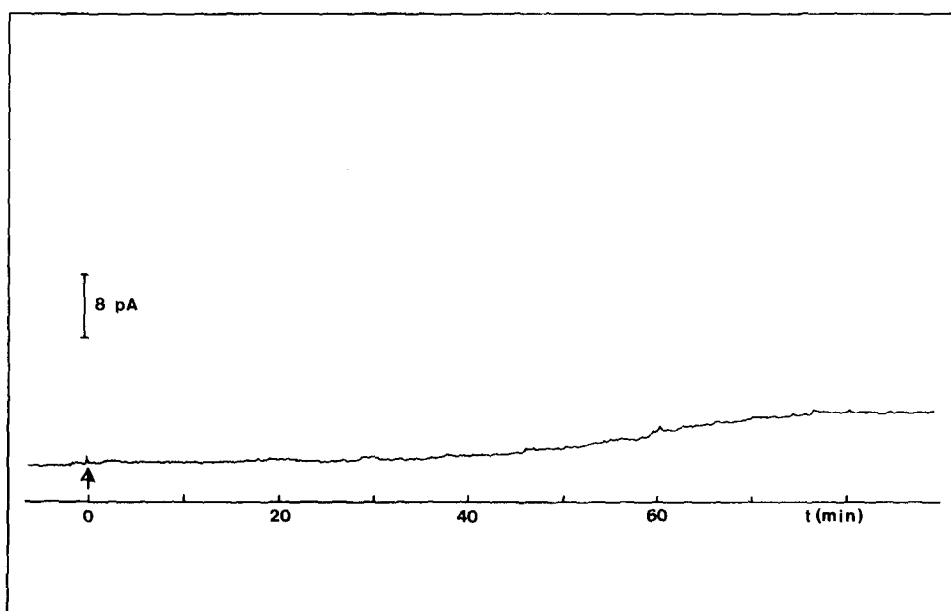


Fig. 2. Chromatogram of the blank GC-MS analysis. Temperature programme, linear from 20°C at 4°C/min.

chromatogram is shown in Fig. 3. As can be seen, minor amounts of some frequently occurring organics were detected. Based on the experimentally determined flame ionization detector response for benzene (1 pA for 2.4 ng of benzene), it was calculated that head-space concentrations of individual organics evolved from the raw materials were less than 5 ppb (v/v).

TABLE I

RESULTS OF THE GC-MS IDENTIFICATION OF VOLATILES IN THE HEAD SPACE OF THE RAW MATERIALS

<i>Compound</i>	<i>Distilled water</i>	<i>Phosphate rock</i>	<i>Water plus HCl</i>	<i>Water plus H₂SO₄</i>
1 Acetone	×	×	×	×
2 Pentene				×
3 Dichloromethane	×			×
4 2-Methylpentane				×
5 3-Methylpentane				×
6 Chloroform	×			×
7 Benzene	×	×	×	×
8 Heptane				×
9 Toluene	×	×	×	×
10 Tetrachloroethene	×			
11 Ethylbenzene	×			×
12 <i>m,p</i> -Xylene	×			×
13 <i>o</i> -Xylene	×			×

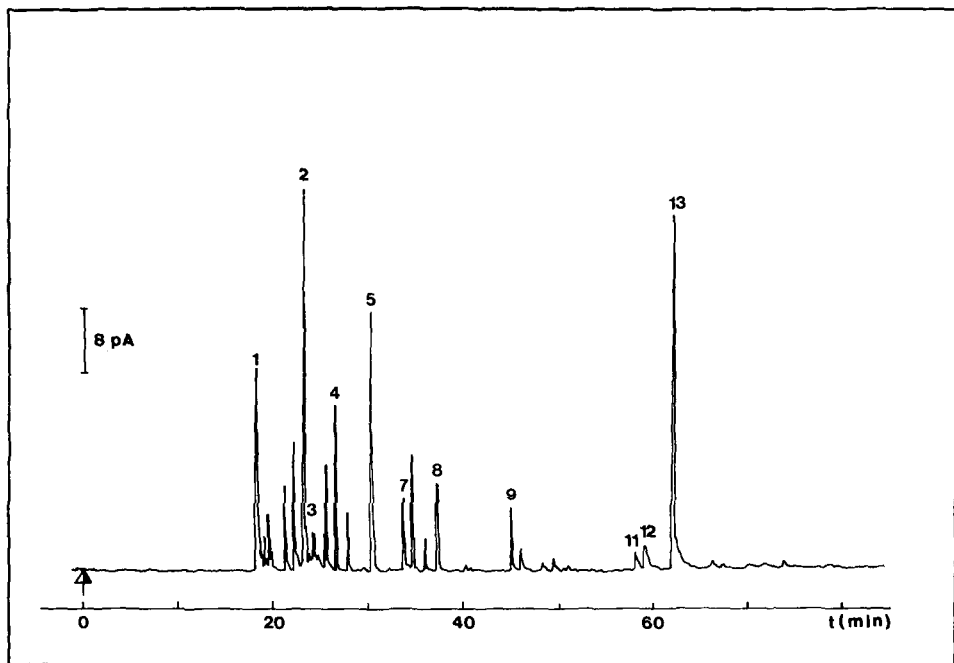


Fig. 3. Chromatogram of the GC-MS analysis of one of the raw materials (sulphuric acid-distilled water). Peak numbers refer to Table I.

Identification of volatiles in acid-treated phosphate rock

A typical chromatogram of the GC-MS analysis of the volatiles liberated during acid treatment of phosphate rock sample is given in Fig. 4. Results of the identification are given in detail in Tables II and III. In order to have a good picture of

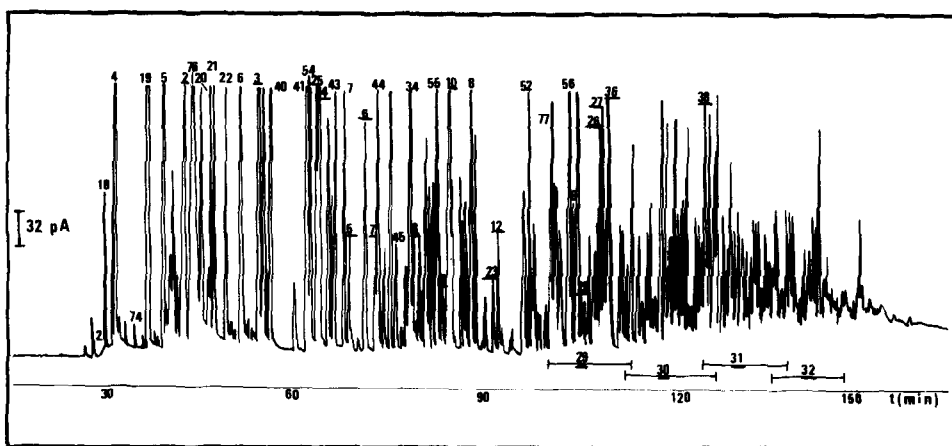


Fig. 4. Chromatogram of the identification of volatiles liberated during treatment of phosphate rock with hydrochloric acid. Temperature programme, linear from 20°C at 2°C/min to 220°C. Normal digits refer to Table II, underlined digits refer to Table III.

TABLE II

NON-ORGANO SULPHUR COMPOUNDS IDENTIFIED BY GC-MS IN THE HEAD SPACE OF ACID-TREATED PHOSPHATE ROCK

I_p = Kovats retention index. In column 1, symbols have the following meaning: S, peak height less than 32 pA; M, peak height between 32 and 320 pA; L, peak height greater than 320 pA. In column 2, × means that the retention index was confirmed by the injection of an authentic sample; n.d. not determined.

Compound	I_p	Phosphate rock treated with		1	2
		H_2SO_4	HCl		
(I) Silicon compounds					
(1) Silicon tetrafluoride	< 400	×	×	S	
(2) Dimethyl silicon difluoride	< 400	×	×	S	
(3) Trimethyl silicon fluoride	416	×	×	S	
(II) Hydrocarbons					
(A) Linear aliphatic					
(4) Butane	400	×	×	L	×
(5) Pentane	500	×	×	L	×
(6) Hexane	600	×	×	L	×
(7) Heptane	700	×	×	L	×
(8) Octane	800	×	×	M	×
(9) Nonane	900	×	×	M	×
(10) Decane	1000	×	×	M	×
(11) Undecane	1100	×	×	M	×
(12) Dodecane	1200	×	×	M	×
(13) Tridecane	1300	×	×	M	×
(14) Tetradecane	1400	×	×	M	×
(15) Pentadecane	1500	×	×	S	×
(16) Hexadecane	1600	×	×	S	×
(17) Heptadecane	1700	×	×	S	×
(B) Branched aliphatic					
(18) 2-Methylpropane	< 400		×	M	
(19) 2-Methylbutane	467	×	×	M	×
(20) 2,3-Dimethylbutane	560	×	×	L	×
(21) 2-Methylpentane	566	×	×	L	×
(22) 3-Methylpentane	580	×	×	L	×
(23) 2,2,3-Trimethylbutane	627	×		M	×
(24) 2,4-Dimethylpentane	667	×	×	M	×
(25) 3-Methylhexane	672	×	×	L	×
(26) 2,5-Dimethylhexane	728	×		M	×
(27) 2,3-Dimethylhexane	760		×	M	×
(28) 3-Methylheptane	766	×	×	M	×
(29) 3,4-Dimethylhexane	770	×	×	M	×
(30) 2-Ethylhexane	775		×	M	×
(C) Aliphatic unsaturated					
(31) 1-Butene	< 400		×	S	×
(32) 2-Methylpropene	409		×	S	×
(33) 2-Butene (<i>trans</i>)	421		×	S	
(34) 3-Butene (<i>cis</i>)	456		×	S	
(35) 1-Pentene	485	×		L	×
(36) 2-Methyl-1-pentene	590	×		M	
(37) Methylcyclopentene	650	×		S	
(38) 1-Propylcyclohexene	n.d.	×		S	

TABLE II (continued)

Compound	Ip	Phosphate rock treated with		1	2
		H ₂ SO ₄	HCl		
(D) Aliphatic cyclic					
(39) Cyclopentane	572	×		M	×
(40) Methylcyclopentane	628	×	×	L	×
(41) Cyclohexane	666	×	×	L	×
(42) 1,3-Dimethylcyclopentane (<i>cis</i>)	686	×	×	M	×
(43) 1,3-Dimethylcyclopentane (<i>trans</i>)	690	×	×	L	×
(44) Methylcyclohexane	725	×		L	
(45) Ethylcyclopentane	734	×	×	L	
(46) 1,2,3-Trimethylcyclopentane	740	×	×	M	
(47) 1,2,3-Trimethylcyclopentane	747	×	×	S/M	
(48) 1,2-Dimethylcyclohexane	785	×	×	S	
(49) 1,2-Methylethylcyclopentane	792	×	×	M	
(50) 1,2-Methylethylcyclopentane	794	×	×	M	
(51) Isopropylcyclopentane	810	×		M	
(52) Ethylcyclohexane	840	×	×	L	
(53) Isopropylcyclohexane	908	×		L	
(E) Aromatic					
(54) Benzene	666	×	×	L	×
(55) Toluene	771	×	×	L	×
(56) Ethylbenzene	870	×	×	L	×
(57) <i>m,p</i> -Xylene	876	×	×	L	×
(58) <i>o</i> -Xylene	900	×	×	L	×
(59) Isopropylbenzene	933	×		M	×
(60) Propylbenzene	964	×	×	L	×
(61) 1-Ethyl-3-methylbenzene	969	×		M	×
(62) 1-Ethyl-4-methylbenzene	970	×	×	M	×
(63) 1,3,5-Trimethylbenzene	976	×	×	M	×
(64) 1-Ethyl-2-methylbenzene	988	×		M	×
(65) 1,2,4-Trimethylbenzene	1001	×	×	M	×
(66) 1,2,3-Trimethylbenzene	1033	×		M	×
(67) Benzene-C ₄	n.d.	4 isomers	3 isomers		
(68) Indane	n.d.	×		S	
(69) Ethylindane	1210	×		M	
(70) Benzene-C ₆	1238	×		S	
(71) Benzene-C ₅	1302	×		S	
(72) 2-Methylnaphthalene	1327	×		S	
(73) 1-Methylnaphthalene	1345	×		S	

the composition of the mixture of volatiles, compounds were classified according to their chemical nature and then in order of elution from the GC column. It is indicated in the tables whether or not the identification was based on MS alone or on the combination of mass spectra and retention data, obtained either from the literature or by analysing authentic samples. No quantitative determinations were performed but, based on peak heights, an indication of the amount of compounds is given.

Since, in the industrial process, phosphate rock is usually treated with sulphuric acid, this acid was also used in the first experiments. GC-MS analyses of the head-space volatiles revealed the presence of a few silicon fluorides as well as numerous hydrocarbons and organic sulphur compounds. Since it was not clear whether the

TABLE III

ORGANOSULPHUR COMPOUNDS IDENTIFIED IN THE HEAD SPACE OF ACID-TREATED PHOSPHATE ROCK

For the meaning of the symbols see Table II.

Compound	Ip	Phosphate rock treated with		1	2
		H ₂ SO ₄	HCl		
(I) Mercaptans					
(1) Methanethiol	n.d.	(x)		L	
(II) Sulphides					
(A) Acyclic					
(2) Dimethyl sulphide	527	x	x	L	x
(3) Ethyl methyl sulphide	617	x	x	L	x
(4) Isopropyl methyl sulphide	676	x	x	L	x
(5) Diethyl sulphide	704	x	x	M	x
(6) Methyl propyl sulphide	717	x	x	M	x
(7) Methyl <i>tert.</i> -butyl sulphide	725		x	S	
(8) Ethyl isopropyl sulphide	754	x	x	S	
(9) Methyl isobutyl sulphide	776		x	S	
(10) Ethyl propyl sulphide	782	x	x	L	
(11) Methyl <i>sec.</i> -butyl sulphide	805	x		S	
(12) Methyl butyl sulphide	820	x	x	M	
C-6 sulphides					
(13) Isomer a	845	x	x	S/M	
(14) Isomer b	849		x	S	
(15) Isomer c	857	x	x	S/M	
(16) Isomer d	876	x	x	S/M	
(17) Dipropyl sulphide	877	x	x	S/M	x
(18) Isomer f	886		x	M	
C-7 sulphides					
(19) Isomer a	n.d.	x		S	
(20) Isomer b	n.d.	x	x	S/M	
(21) C-8 sulphide	n.d.	x		S	
(22) C-10 sulphide	1296	x		S	
(B) Cyclic					
(23) Thiacyclopentane	815	x	x	S	x
(24) Thiacyclohexane	860	x	x	M	x
(25) 2-Methylthiacyclopentane	879	x	x	S	
(26) 2,5-Dimethylthiacyclopentane	890	x	x	M	
(27) 2,5-Dimethylthiacyclopentane	895	x	x	M	
(28) 2-Methylthiacyclohexane	910	x	x	M	x
(29) Cyclic isomers with structure C ₆ H ₁₂ S	890-1000	x	x	M-S	
(30) Cyclic isomers with structure C ₇ H ₁₄ S	950-1050	x	x	M-S	
(31) Cyclic isomers with formula C ₈ H ₁₆ S	1000-1100	x	x	M-S	
(32) Cyclic isomers with formula C ₉ H ₁₈ S	1050-1250	x	x	M-S	
(33) Cyclic isomers with formula C ₁₀ H ₂₀ S	1200-1350	x	x	M-S	
(III) Disulphides					
(34) Dimethyl disulphide	752	x	x	L	x
(35) Ethyl methyl disulphide	872	x		M	x
(36) Isopropyl methyl disulphide	899	x	x	M	
(37) Diethyl disulphide	903	x	x	M	x

TABLE III (continued)

Compound	Ip	Phosphate rock treated with		1	2
		H ₂ SO ₄	HCl		
(IV) Thiophenes					
(38) Trimethylthiophene	n.d.	×			S
(39) Thiophene-C ₄	n.d.	3 isomers	1 isomer		S
(40) Thiophene-C ₅	1209	×			S
(41) Thiophene-C ₆	1279	×	×		S

nature of the mineral acid was determining the identity of the head-space volatiles, a number of treatments with hydrochloric acid were also performed; as can be seen from Tables II and III, only minor changes in the composition of the head space were observed. So it was concluded that the nature of the mineral acid was not influencing the identity of the head-space volatiles.

Three silicon compounds were identified in the head space of acid-treated phosphate rock. Silicon tetrafluoride was easily recognized by the presence of an intense fragment at m/e 85 and isotopic peaks at m/e 86 and m/e 87. Dimethyl silicon difluoride and trimethyl silicon fluoride showed characteristic peaks at m/e 81 and m/e 77, respectively. Silicon tetrafluoride and hydrogen fluoride are well-known by-products of phosphate treatment. To prevent the emission of these compounds, industrial gases are usually scrubbed with water, which yields a diluted orthosilicic acid solution. Hydrogen fluoride was not detected during the GC-MS analyses, probably because of its low molecular weight.

Assuming the same detector response for all volatiles, 75% of the mixture consisted of hydrocarbons. Linear, branched, unsaturated, and cyclic aliphatic and aromatic hydrocarbons with boiling points ranging from 0 to 300°C were detected. The identification of these compounds by their mass spectra was generally straightforward, although for isomeric structures retention data were used to confirm the interpretation of the spectra.

All other volatiles in the mixture were organosulphur compounds, belonging to different classes: a mercaptan, acyclic and cyclic sulphides, disulphides and alkyl thiophenes. Methylmercaptan was detected in two of the nine samples of phosphate rock treated with sulphuric acid and not in samples treated with hydrochloric acid. Therefore this compound seems to be present rather sporadically.

Acyclic sulphides up to diethyl sulphide were identified by MS alone. Owing to the rapidly increasing number of possible isomeric structures, the combination of mass spectra and retention data was necessary to identify higher sulphides. Cyclic sulphides showed rather prominent molecular ions in the series with m/e 88 + 14N. Alkyl-substituted thiacycloalkanes often produce base peaks by splitting of the alkyl branch: thus thiacyclopentanes produce a base peak at m/e 87 and thiacyclohexanes at m/e 101. The elimination of an alkene fragment from the ring structure was also observed, and resulted in a typical fragment at m/e 74 (C₃H₆S⁺). Throughout the chromatograms cyclic structures with formulac from C₄H₈S to C₁₀H₂₀S were detected. In most cases it was not possible to indicate the exact isomer because of the

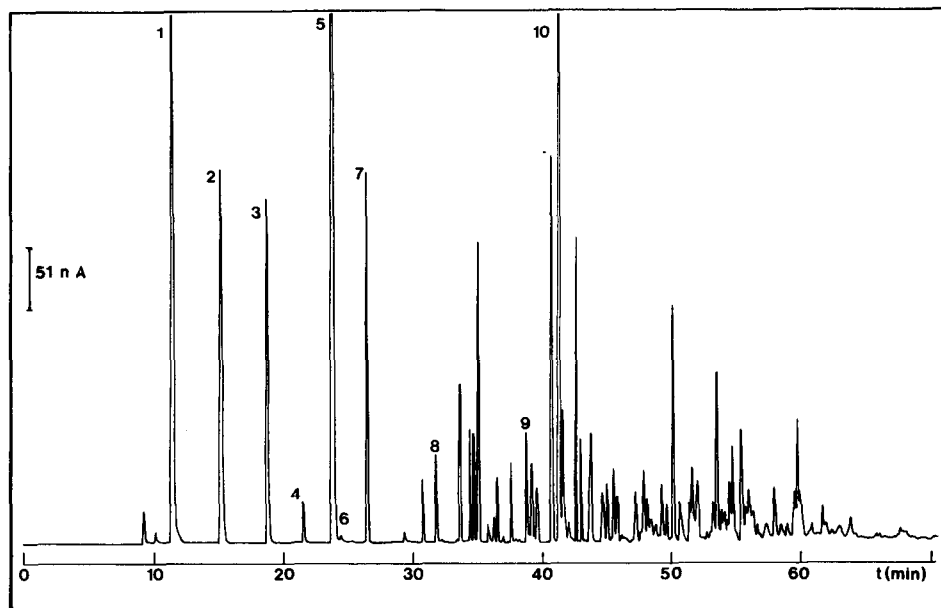


Fig. 5. Chromatogram of the GC-FPD analysis of volatiles in the head space of acid-treated phosphate rock. Temperature programme: linear from 20°C at 2°C/min. Peaks: 1 = dimethyl sulphide; 2 = ethyl methyl sulphide; 3 = isopropyl methyl sulphide; 4 = diethyl sulphide; 5 = dimethyl disulphide; 6 = isopropyl ethyl sulphide; 7 = ethyl propyl sulphide; 8 = thiacyclopentane; 9 = thiacyclohexane; 10 = isopropyl methyl disulphide.

great numbers of possible isomers (*e.g.* a cyclic sulphide with formula $C_7H_{14}S$ and with at least a five ring gives 59 isomers) and because of the lack of reference compounds.

Four disulphides and some alkyl thiophenes were identified in the head space of phosphate rock treated with sulphuric acid or hydrochloric acid.

In order to confirm GC-MS results, 2-methylthiacyclohexane, three disulphides and three asymmetric sulphides were synthesized. The mass spectra of the synthesized compounds were in good agreement with the spectra of the compounds in the samples. The following retention indices were calculated for the synthesized compounds: ethyl methyl sulphide, 617; isopropyl methyl sulphide, 676; methyl propyl sulphide, 717; 2-methylthiacyclohexane, 910; ethyl methyl disulphide, 872; isopropyl methyl disulphide, 899; methyl propyl disulphide, 912.

Finally, to obtain a chromatogram in which the interference of hydrocarbons and organic sulphur compounds would be at a minimum, five samples were analysed by GC-FPD; a typical chromatogram is given in Fig. 5. The GC-FPD apparatus was not coupled with the mass spectrometer. Therefore dimethyl sulphide, dimethyl disulphide and isopropyl methyl disulphide, which were the most abundant organosulphur compound peaks in the GC-MS analyses, were used to calculate the retention indices of other organosulphur compounds in the GC-FPD chromatograms. These chromatograms confirmed that numerous sulphur compounds are present in the head space of acid-treated phosphate rock and that, within this class of com-

pounds, dimethyl sulphide, dimethyl disulphide, isopropyl methyl disulphide, ethyl methyl sulphide and ethyl propyl sulphide are the most abundant compounds. As far as the abundance of the different classes of organosulphur compounds is concerned, the following figures were measured (as a percentage of the total FID-integrated signal): acyclic sulphides, 15%; cyclic sulphides, 6.7%; disulphides, 2.7%; and thio-phenes, 0.5%.

CONCLUSION

GC-MS identification of volatiles in the head space of acid-treated phosphate rock revealed the presence of some organosilicon compounds and numerous hydrocarbons and organosulphur compounds. A mercaptan, acyclic and cyclic sulphides, disulphides and alkylthiophenes were identified. The presence of organic compounds in phosphate rock is in accordance with the generally accepted theory that phosphogenic events are associated with a high organic productivity⁸.

Since the human olfactory system is about 1000 times more sensitive for sulphur compounds than for hydrocarbons, the sulphur compounds identified are probably responsible for the odour problems caused by acid treatment of phosphate rock.

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