

Emission of the odour substances from fertilizer industry

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Mineral fertilizers are indispensable for the intensification of plant production in agriculture. This process can cause a significant odour nuisance for the environment due to organic compounds content in apatites and phosphorites converted into fertilizers. The following chemical compounds are emitted to the gas phase among others: hydrogen sulphide, organic sulphides and (methyl, ethyl, isopropyl, butyl) disulphides, chain hydrocarbons, organic oils, waxes and carboxylic acids. A method using gas chromatography analysis with the mass detector (TD-GS-MS), to determine trace concentrations, was developed and tested for the assessment of odour nuisance substances emission from these processes. Application of additional thermal desorber to enable the intense desorption of the investigated organic compounds (previously adsorbed on classical sorbents) in the industrial research has been taken into consideration. In effect it facilitates the accumulating substances to be analyzed at short time interval providing identifying measurements. The technique has been verified during the investigation of the substances emitted in fertilizers processes at Maroko phosphorite decomposition. The organic sulfur compounds, aliphatic and aromatic hydrocarbons have been detected.

Keywords: odours, mineral fertilizers.

INTRODUCTION

Mineral fertilizers, applied in large amounts in agriculture, are produced in the chemical technological processes in which mineral resources are transformed. Technologies that use phosphorites as a raw material have remarkable influence on the odour nuisance of these processes. Phosphorites belong to the sedimentary rocks. Biological processes occurring in aqueous and land environment were of great importance for originating, further transformations and accumulation of these minerals (Fig. 1). These processes proceeded through direct or indirect participation of living organisms. The largest amounts of phosphates precipitated into the solid phase were produced in aqueous environment with the activity of the following factors: concentration of withered organic matter of organism origin, occurrence of temperature gradients in aqueous environment (e.g. caused by water streams mixing), concentration of other chemicals like chlorides, carbon dioxide as well as pH value.

Diversity of environmental conditions had an influence on significant crystallographic changes as well as alteration in chemical composition and physicochemical characteristics of the currently exploited phosphate ore¹⁻³. It also affects the large versatility in the organic substances range (Table 1). Depending on the chemical compounds structure the following substances can be distinguished^{1, 3, 4}:

- long chain hydrocarbons (undecane, tetradecane, pentadecane, hexadecane),
- porphyrine,
- nitrogen compounds containing pyrrole ring,
- aliphatic carboxylic acids,
- fats,
- waxes,
- alkyl benzene sulphonic acid, isopropyl naphthalene sulphonic acid,

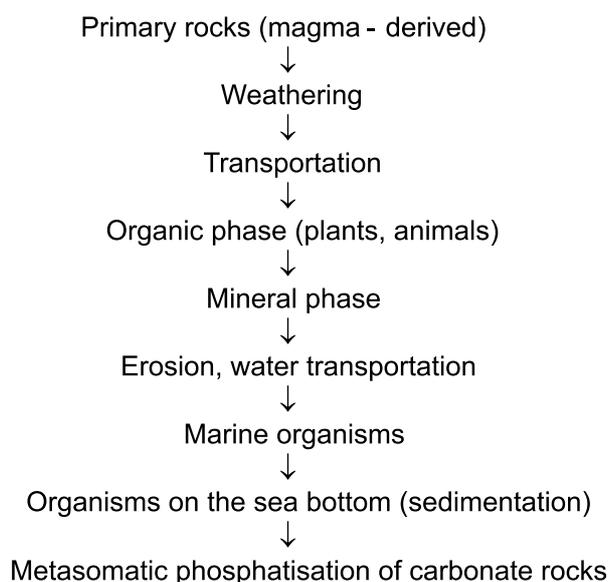


Figure 1. The geochemical forming of phosphorus raw materials

– sulfides (ethyl methyl sulfide, isopropyl methyl sulfide diethyl and dimethyl sulfide, ethyl isopropyl sulfide, 3-pentanethiol, CS₂, ethyl sulfide),

– disulfides (1-methyl-ethyl-propyl, dimethyl ethyl, hexyl-1-ethyl, 3-methyl ethyl-2-methylpropyl, butyl-2-methylpropyl, 3-methylbutyl-n-pentyl, n-amyl-2-methylpropyl, di-3-methylbutyl, di-1-methylpropyl, di-n-pentyl, dipentyl, n-butyl-n-hexyl).

Concentration of organic compounds, in the phosphorus raw materials, did not affect the technological conditions of phosphorus raw materials processing significantly. Excessive foaming and occurrence of permanent foam on the surface of reactive pulp in reactors is eliminated mechanically: through the application of special mixers

Table 1. Concentration of organic substances in phosphorous raw materials^{2, 5}

Phosphorous raw material	Concentration of organic compounds mass % of C
Florida (USA)	0.15 – 0.60
North Carolina – Lee Creek (USA)	0.15 – 1.60
Khouribga (Morocco)	0.21 – 0.26
Youssoufia (Morocco)	0.46 – 1.00
El Hassa (Jordan)	0.20 – 0.29
Dagbati (Togo)	0.14 – 0.20
Taiba (Senegal)	0.37 – 0.57
Nauru (Nauru)	1.13
Phalaborwa (Republic of South Africa)	0.03
Tapira (Brasil)	0.07 – 0.09
Djebel Onk (Algeria)	0.30
Jamarkotra (India)	0.27
Mdilla (Tunisia)	0.80

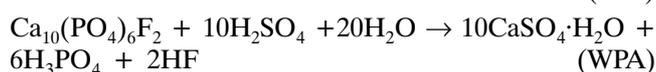
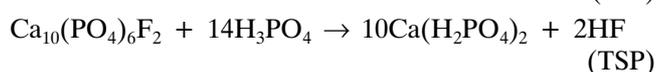
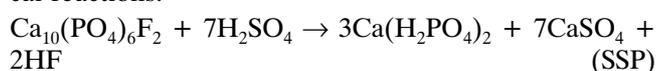
construction fitted with paddles; as well as chemically: through adding the substances that decrease foams durability. An essential problem is the gray-brown colour of the phosphoric acid solution, obtained from the initial phosphorous raw material, which is characterized by an excessive concentration of organic compounds. The white colour is the requirement in the case of the usage of this product for the phosphorous compounds production, designed for application as fodder phosphates or the production of household cleaning agents. The demand mentioned above caused technological elimination of this unfavourable feature. The problem has been solved using preliminary high-temperature calcinations of raw materials, polluted with the organic compounds, or the removal of the colour-causing organic substances from the manufactured phosphoric acid solution by the adsorption method. Unfortunately, it is correlated with relatively high processing costs^{6, 7}.

A different kind of problem, which has gained significance in recent years, is the odour nuisance – connected with the industrial processing of phosphorous raw materials. In spite of the reduction of volatile fluorine and SO_x compounds emission, chemicals that were thought to be the most harmful gaseous pollutions so far, undesirable odours, which occur in surroundings of industrial phosphorous raw materials processing installations, are still the cause of people complaints about the quality of the environment. These substances are being associated with health hazard and also cause distinct social discomfort. Formal-legal requirements for the highest concentrations of gaseous air pollution in Polish law, relating to the selected chemicals, including the odour generating substances, are defined in a special decree containing fixed indexes⁸. These duties result from the Law on Environmental Protection bill⁹. Obligatory indexes determine the acceptable levels of air pollution. However, according to experts, unpleasant smells sensation is a more complexed phenomenon. This process is connected with the structure and physiology of the signals by the olfactory receptors, sensors of the nervous system. The impulse, generated in these organs, is subsequently converted in brain by complexed biological and biochemical processes leading to obtaining appropriate human responses. Therefore, in

many European countries, including Poland, intensive work is conducted to establish a special bill preventing society from the effect of malodorous gases emitted to atmosphere, efficiently.

METHODOLOGY FOR THE IDENTIFICATION OF SUBSTANCES EMITTED BY THE FERTILIZER INDUSTRY

Damaging the apatite structure of the phosphorous raw material is the primary process implemented by the fertilizer industry. During this stage the odour generating gas pollutants, are emitted to gas phase. It occurs in the phosphorite degradation process using mineral acids (sulfuric acid, phosphoric acid), single superphosphate production (SSP), triple superphosphate production (TSP) as well as phosphoric acid (WPA) produced by the degradation of the phosphorous raw material with sulfuric acid¹⁰. These processes can be characterized with the following chemical reactions:



The investigations have been made on the analysis of gases emitted during a single superphosphate production process. The gas phase samples have been collected from the stream of gases directly after reaction between phosphoric acid and Morocco phosphorite (Fig. 2). Chemical composition of the applied phosphorite is shown in Table 2.

Samples of post-reaction gases have been collected before the absorbing module. These are the representative samples that characterize gases arising during the phosphorous raw material degradation process. Samples have been taken with the usage of the pump-forced (Pocket

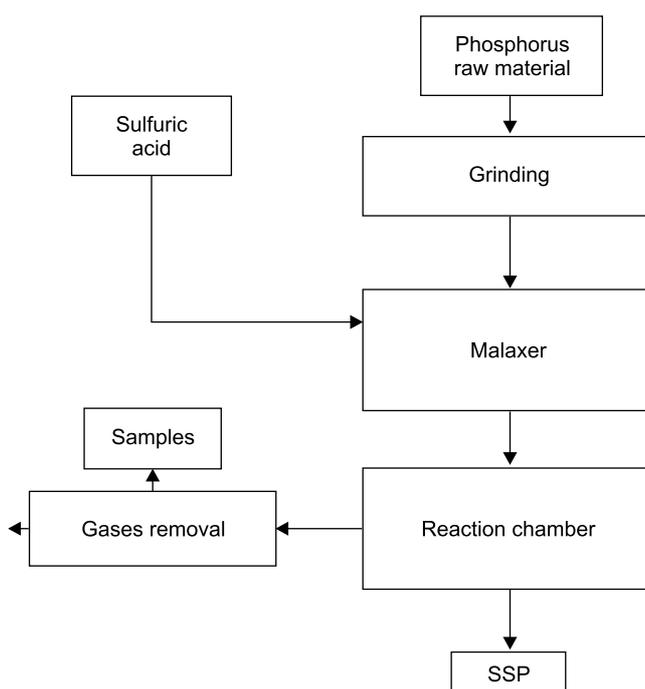
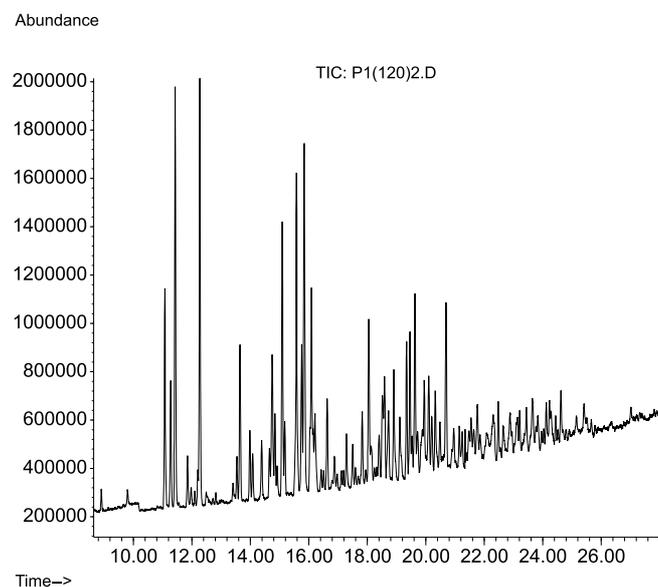
**Figure 2.** Collecting samples of gases emitted in a single superphosphate production process

Table 2. Chemical composition of phosphorite Morocco, applied in the single superphosphate production

Component	Unit	Concentration
P ₂ O ₅	mass %	31.15
CO ₂	mass %	6.44
SO ₃	mass %	1.62
CaO	mass %	51.05
MgO	mass %	0.44
Fe ₂ O ₃	mass %	0.27
Al ₂ O ₃	mass %	0.41
F	mass %	3.62
Corg	mass %	0.24
Cd	mg/kg	23.1
As	mg/kg	13.5
Hg	mg/kg	0.95
Pb	mg/kg	4.45

Pump 210 (SKC) calibrated gas flow through the absorption pipe filled with hydrophobic sorbent, specific for gaseous organic compounds, of Tenax TA/Carbograph1 TD type. Samples have been collected at times 8, 15, 30, 60 and 120 minutes, using flow intensity of 100 and 200 ml/min. Gathered samples have been analyzed with methodology based on gas chromatography (TD-GC/MS), modified for these research purposes. TD-GC-MS allow determining the qualitative as well as the quantitative trace amounts of gas compounds in the gaseous samples. Low concentration of the organic pollution in gases emitted from fertilizer industry has been submitted with the special procedure that utilizes the chromatographic analysis stand extended with the thermal desorber. Thermal desorption relies on the desorption of gaseous compounds from the sorbent to the heated stream of gas and transportation of the analyte to gas chromatograph. This process follows in two steps:

– desorption of the analyte from the adsorption pipe which was used to collect the investigated components of industrial gases and subsequent adsorption in the intermediate pipe at low temperature (cold trap),

**Figure 3.** The results of TD-GC/MS chromatographic analysis of the samples of gases gathered from superphosphate production (column: HP-VOC, 60m length, diameter of 0,2mm, initial temperature 40°C, rate of growth: 5°C/min to 200°C)**Table 3.** Chemical compounds that occur in gases obtained from superphosphate production

Retention time [min]	Name of compound	Concentration
8.90	Hexane	*
9.80	2,4-dimethylpentane	*
11.08	2-methylhexane	***
11.28	2,3-dimethylpentane	***
11.43	3-methylhexane	***
11.85	3-ethylpentane	*
12.27	heptane	***
13.65	methylcyclohexane	***
13.98	Ethylcyclopentane	**
14.07	1,2,4-trimethylcyclopentane	**
14.39	1,2,3-trimethylcyclopentane	**
14.74	2-methylheptane	***
14.85	4-methylheptane	**
14.91	Dimethyl disulfide	*
15.09	3-methylheptane	***
15.18	3-ethylhexane	**
15.58	Toluene	***
15.76	1,3-dimethylcyclohexane	**
15.84	2-methylthiobutane	***
16.09	Octane	*
16.50	ethylpropylsulfide	***
16.63	1,2-dimethylcyclohexane	*
17.29	1-methylthiobutane	**
17.83	propylcyclopentane	**
18.05	ethylcyclohexane	**
18.52	Methyl ethyl disulfide	***
18.72	1,2,4-trimethylcyclohexane	**
19.11	2-methyltetrahydrothiophen	**
19.34	ethylbenzene	**
19.46	2-methyl-3-methylthiobutane	***
19.63	Xylene	**
19.95	Nonane	**
20.21	1-ethyl-4-methylcyclohexane	**
20.32	2,5-dimethyltetrahydrothiophen	**
20.69	Methyl isopropyl disulfide	***
21.77	propylcyclohexane	*
24.22	dimethyl trisulfide	*
24.63	Methyl sec-butyl disulfide	**

– releasing the analyte from cold trap with the usage of temperature impulse and transferring into gas chromatograph.

Following this procedure, the substances adsorbed at optimal, selected in accordance with the conditions and their specific character, period of time, are being desorbed and sorbed again on the intermediate sorbent. Then these substances are being desorbed using temperature impulse increase and transferred into the measurement part of gas chromatograph. Thus the effect of the applied procedure is an accumulation of the investigated substances in the analysed gas. This effect improves the capabilities of both the qualitative and quantitative pollution analysis. HP-VOC chromatographic column (60m length, diameter of 0.2mm, diameter of filling sorbent of 1.1µm) was used for the samples (collected from superphosphate installation) testing. Helium, flowing through the column with the intensity of 0.9 ml/min, has been applied as a carrying gas. The results of the TD-GC/MS analysis of the samples collected from the superphosphate installation have been shown in Figure 3. The identified substances and rated levels of their concentration have been presented in Table 3.

RESULTS DISCUSSION AND CONCLUSIONS

The applied procedure of collecting and analysis of gases samples, from a single superphosphate production installation allowed the identification of the large group of organic compounds. Part of these chemicals found to possess disadvantageous influence on the malodorous properties of the phosphorous fertilizers industry. Sulfur organic compounds, at least half of all the identified compounds, play the dominant role in this influence. Among them sulfur compounds of sulfides, disulfides, alkyl trisulfides and tetrahydrothiophen methyl derivatives type possess the odour-generating properties. Aliphatic and cyclic hydrocarbons (pentane, cyclopentane, hexane and its methyl derivatives, heptane, nonane) as well as aromatic hydrocarbons (benzene, toluene, ethylbenzene, xylene), identified in the investigations, have also unfavorable influence on the malodorous profile.

LITERATURE CITED

1. Slack, A.V. (1968). *Phosphoric acid*, Marcel Dekker Inc., New York.
2. Impurities in Phosphate Rock (1990). *Fert. Int.* 283, 27 – 31.
3. Mair, A.D. (1985). *Organic matter and sulfur distribution in phosphorites*, National Fertilizer Development Center, Muscle Shoals.
4. Kośmider, J., Mazur Chrzanowska, B. & Wyszyński, B. (2002). *Odours*, Wyd. Nauk. PWN, Warszawa. (in Polish)
5. Becker, P. (1989). *Phosphates and phosphoric acid*, Marcel Dekker Inc., New York.
6. Hanna, A.A. & Ali A.F. (1992). Removal of organic matter from crude wet-process phosphoric acid, *J.Chem. Tech. Biotechnol.* 55, 205 – 208.
7. Mellah, A., Silem, A., Bonalia, A. & Koda, R. (1992). Adsorption of organic matter from a wet phosphoric acid using activated carbon: Equilibrium study, *Chem.Eng.Proc.* 3, 191 – 194.
8. Ministry of Environmental Decree from 5 December 2002 in matter of value of references for some substances in air (2003). *Dz. U.*, 2003, 1, 12. (in Polish)
9. The Protection of Environment Law from 27 April 2001 (2006). *Dz. U.* 2006, 129, 902. (in Polish)
10. Lowrison, G.Ch. (1989). *Fertilizer Technology*, Ellis Horwood Limited, Chichester.