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IDENTIFICATION OF ODOUR-GENERATING SUBSTANCES IN PHOSPHATE ROCK PROCESSING OPERATIONS

IDENTYFIKACJA ZWIĄZKÓW ODOROTWÓRCZYCH W PROCESACH PRZETWARZANIA SUROWCÓW FOSFOROWYCH

Abstract: There is no kind of odour control law in Polish legislation. Therefore, Polish citizens and many branches of industry have got problems which are connected with the influence of volatile chemical substances which affect the drop of air quality. Couples of government attempts of solving this situation by proposing suitable projects were rejected by industry and scientist. The phosphate ores manufacturing especially superphosphate production was chosen as an example of a branch of industry which is a source of odours. In due to characterize odour problem in the light of superphosphate production the exhaust gases were analyzed and the results were compared with reference to professional literature. The gas samples were taken in FOSFAN S.A Company during superphosphate manufacturing and analyzed using TD-GC/MS method. There were identified over 80 volatile organic compounds like alkanes, cycloalkanes and aromatic compounds. Probably the most significant influence for odour perception is connected with presence of sulphur volatile organic compounds. In addition to lack of professional data connected with smell of gas mixture consisted with different particles there is no possible to exclude the influence of other particles for human smell perception. Finally the new method of further research was suggested. This research includes not only analysis of organic matter in waste gases but also in phosphate rocks and superphosphate fertilizer. To obtain comparable results the whole research should be provided during the same day of production. This sort of research could give a solution for deodorization and preventing the drop of air quality. It could be also helpful in course to develop new law projects. It is predicted that in future the production of superphosphate fertilizer will increase. Thereby the greater amount of odours will be released into the atmosphere. That is why further research combined with creating well functioning odour control law is so important to be established.

Keywords: odours, super phosphate, volatile organic compounds

The notion of odour-generating substances is very wide as malodorous compounds are very complex group of chemical particles. Mostly these chemicals differ as for the

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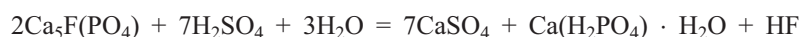
odour and their mixtures can have very diversified and often unpredictable odours. This is why the presence of malodorous compounds in the air possess many problems starting from their identification and determining their concentration and finishing with selecting the method of their neutralization. As manufacturing companies are developing, more and more people complain to various bureaus about too much drop in air quality. This issue has become a ranging problem and the lack of projects which could solve it is making things worse. There is a noticeable gap in Polish legislation as there is no law which would regulate in comprehensive way the problems of odour-generating compounds presence in the air. The suggested solutions concerning the possible concentration of odour-generating compound in the air and the resulting norms and rules creation are based on the odour analysis carried out by panel of qualified people who are sensitive to odours. The test is done several times but still it depends on subjective judgment of panel members. Such judgment, according to latest assumptions of "odour bill" draft, is to be a foundation to carry penalty on the manufacturers, or even either stopping the production or closing the factories by local authorities. It has not been mentioned how one can check and control the decisions of authorities. According to the assumptions of bill draft local authorities will not need to consult the specialist in the field of odour nuisance before imposing restrictions on given company. Polish Confederation of Employers does object to this form of bill as it might cause more problems than solutions. Next projects or assumptions suggested by Ministry of Environment should include some alternative solution to such stalemate which will derive ideas from ready made and running "odour bills" that are effective in for example Holland or Japan. However, the way of specifying permissible concentration of odour in the air is not the only barrier that obstructs the accomplishment. Next problem is the cost of pilot analysis, laboratory equipment and modernization of manufacturing systems that are the source of odour-generating substances. Literature data says that Poland cannot afford introducing reformation in this field [1–3].

In the majority of countries legal protection of air quality is based on setting reference unit which specifies the amount of odour-generating substances in the air. In EU the European odour unit ou_E is used which is described in norm EN 13725:2003. Moreover, the grade of odour nuisance is generally connected to pointing permissible amount of emission caused by different kinds of odour-generating sources and modelling dispersion of odour-generating substances in the air. The standards of odour quality of the air specify permissible level of odour-generating substance concentration in the air – adequately for the specified concentrations the frequency of their yearly outpass which is often given as percentile of average concentration as the subject to one hour [4, 5].

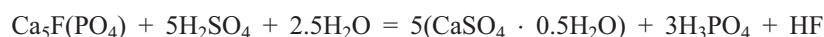
The works on standardization of test methods used in olfactometry are being performed all the time, however, they have different objectives that is why the regulations differ from one another even within EU. The law in this field will not be systemized unless there is a quick possibility of odour assessment which would free the legislator from subjective results obtained by the panel members who specify the concentration of odour-generating compounds using their smell. Maybe the solution lies in creating electronic sensor, colloquially called "electronic nose", that would specify

the odour concentration. The works on such device are in progress in many countries, however, the universal sensor that would specify odour concentration in any conditions have not been created. It is connected to a very complicated mechanism of sensing, identification and memorizing the smells by a human who has not been well-known yet. As we can see, the creation of law that is fully adequate to the nature of the problem is really hard and it might take a few or many years of intensive scientific and specialized work.

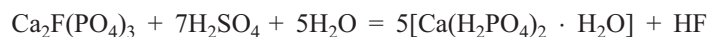
In this elaboration the emphasis was put on the problems of odour nuisance that goes with production of simple superphosphate. Reaction of the degradation of phosphoric raw material containing fluorapatite, as the most essential compound can be introduced as follows:



This reaction is conducted in two successive stages. In the first stage a fluorapatite available on the surface of granules of milled raw material is subjected to degradation. In this stage phosphoric acid is obtained according to an undermentioned chemical reaction [6, 7]



When the sulphuric acid delivered as the substrate ends, the process limits only to the other stage of the fluorapatite acidulation reaction of the following chemical equation:



Reactions of the phosphoric raw materials acidulation with sulphuric and phosphoric acid are exothermic [6]. The superphosphate continues to cure in the store for about 6–8 weeks. Even in the ready product the reaction mentioned above can not achieve the equilibrium, however its rate is very slow.

Phosphate rocks used for the production of simple superphosphate include some amount of organic matter. Exactly these organic compounds, during reaction between sulphuric acid and phosphate rock gives origin for volatile odour-generating substances causing drop of air quality in the surrounding of fertilizer manufacturing plants based on superphosphates.

The concentration of organic compounds in phosphate rocks oscillates in a range of 0.3 % to over 1.7 %. Approximately one fifth of organic compounds is soluble, the insoluble phase is based on kerogenic-type compounds. The kerogenic substances are geopolymers ie heterogeneous organic phase consisting of components of aliphatic, aromatic, ester and lipid character. Part of them contains large amount of sulphur, nitrogen and oxygen, and due to their properties the creation of metal-organic complexes is allowed [8].

Westerlich et al carried out an analysis of organic compounds contained in Tunisian phosphate rocks. The organic compounds were extracted from the phosphate rock samples to methyl chloride and ethyl acetate solutions. The mixtures obtained according

to the following procedure were analyzed using GC/MS methods. Approximately 80 various chemical compounds were detected including aliphatic, aromatic hydrocarbons, paraffines, hydrocarbons containing branched carbon chains, cyclic hydrocarbons, esters, thiols, heterocyclic compounds, lipid acids, amines, carboxylic acids, large amount of sulphur containing compounds as well as steroids and other. The samples of sulphuric acid solution were also analyzed by the same chromatography analysis. Sulphuric acid found to be carrier of organic compounds such as paraffins and esters. However these compounds are not potentially odour-generating [9].

Taking into consideration keeping good relationships with the local community the Chemical Manufacturing Plants producing phosphorus fertilizers are deciding to carry the modernization of production installations out and to establish cooperation with external companies, in order to determine the efficient method of the odour nuisance reduction. One of methods consists in using technical antiodorous preparations for vapouring interior of the chimney-shaped emitter. As a result of specific physico-chemical processes, occurring between malodorous molecules and neutralizing particles, being included in composition of antiodorous preparation, the osmic properties of odorous molecules present in waste gases from chimney-shaped emitter are blocked [10].

Many methods of the deodorisation also exist, using various properties of odour generating substances and technical-exploitation conditions in industrial plants. The part of them was presented in the undermentioned table (Table 1).

Table 1

List of selected methods of the deodorisation [4]

Deodorisation technique	Application	Advantages	Disadvantages
Method invented by Kurmeier, in which an oxidant (chlorine) is introduced to waste gases before entering into the absorber filled up with calcareous stone sprinkled with water	Deodorisation of waste gases from manufacturing plants using animal wastes and from objects of public utilities	Significant effectiveness and low costs of conducting the process	Obtaining large amounts of troublesome sewages
Ozonization	Deodorisation of waste gases from manufacturing plants processing fish, fats, rubber and in chemical as well as pharmaceutical industry	Low costs, waste-free, the possibility of joining with different methods in order to enhance the effectiveness of the process and the easiness of cleaning the installation	A requirement of removing ozone from gasses after deodorisation is a disadvantage of this process
Thermal oxidation	Burning gasses is being used for the deodorisation in coffee incinerators and bitumen manufacturing plants	Simple handling and waste-free	Expensiveness of the exploitation and problems at conducting processes at the change of the temperature of introduced gasses

Table 1 contd.

Deodorisation technique	Application	Advantages	Disadvantages
Sorption-oxidation method consist in joining absorption and thermal oxidation	Deodorisation of gasses containing solvents	Low costs and the unattended handling	High investment costs and the narrow range of applications
Condensation method	Deodorisation of gasses coming from objects of public utilities, animal and agricultural waste-processing plants, the foundry or the paint shop	Low costs	Obtaining unusually troublesome sewages
Masking	The deodorisation of gasses from animal farms, dumps, restaurants or toilets	Low costs, the simple handling, using the chemical compounds safe for the external environment	The high capacity of the ventilation system is required, strong dependence on weather conditions

Compounds being included in antiodorous preparations composition are not toxic for animals, plants and people and are readily biodegradable. Nowadays it is recommended to abandon traditional antiodorous preparations (eg containing aldehydes), which react with functional groups of odour generating substances, as in of such reactions environmental pollutions of the different type can occur. Modern preparations act on the basis of physicochemical processes, rather than of only chemical reactions [10].

Materials and methods

The gas samples were collected from simple superphosphate based fertilizer manufacturing plant. The samples were collected during ordinary working day applying the built in place system of the scheme presented in Fig. 1.

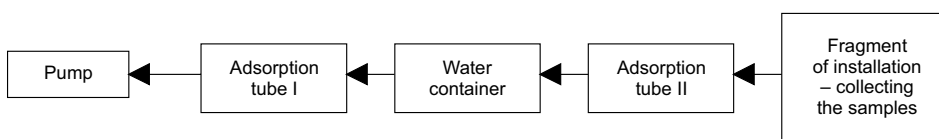


Fig. 1. Scheme of sample collection system

The first tube was filled with Carbosieve SIII adsorbent intended for adsorption of highly volatile compounds nC_2 - nC_5 whereas second tube was filled with Tenax TA/Carbograph1TD adsorbent intended for collecting nC_2 - nC_{26} compounds. The samples were being collected under constant flow rate = $100 \text{ cm}^3/\text{min}$ for 60 minutes. The gas samples were subsequently collected to two plastic containers. Two repetitions of sample collection were carried out. The containers and the tubes with the adsorbed gas were secured and placed for TD-GC/MS method analysis. The TD-GC/MS method

is the gas chromatography using thermal conductivity detector coupled with mass spectroscopy. This method allows for both quantitative and qualitative analysis of volatile compounds in gas samples. For conducting the analysis of collected samples the apparatus with HP-VOC 60 m; 0.2 mm; 1.1 μm) chromatographic column built-in with cold trap U-T6SUL Inert Sulphur Trap ($\text{C}_2\text{-C}_{12}$) was applied. The experiments were made with the initial temperature of 40 $^{\circ}\text{C}$ increasing by 5 $^{\circ}\text{C}$ per minute obtaining 200 $^{\circ}\text{C}$ at the inert gas (He) flow through the column with the flow rate 0.9 cm^3/min and $mz = 15\text{--}200$ applying so-called “cold trap” [11, 12].

Results

The alkanes with the total concentration of 3.970 mg/m^3 found to be the most abundant group of chemical compounds in exhaust gases from manufacturing of simple superphosphate. Another large group of chemicals was cycloalkanes with a total concentration of 1.189 mg/m^3 . Additional two groups of compounds: aromatic hydrocarbons and sulphur chemicals were found to be present at the same concentration range as cycloalkanes, however the aromatic hydrocarbons concentration – 0.657 mg/m^3 – is higher than sulphur chemicals – 0.529 mg/m^3 (Table 2).

Table 2

The sulphur chemicals identified in analyzed samples

No.	Retention time [min]	Name of compound	Concentration [mg/m^3]
1	6.99	dimethyl sulfide	0.019
2	9.50	methylthioethane	0.064
3	11.48	2-methylthiopropene	0.096
4	12.97	1-methylthiopropene	0.052
5	14.54	dimethyldisulfide	0.042
6	15.46	2-methylthiobutane	0.083
7	18.72	2-methyltetrahydrothiophene	0.033
8	19.05	2-methyl-3-methylthiobutane	0.020
9	19.92	2,5-dimethyltetrahydrothiophene	0.045
10	20.08	2-methyltetrahydrothiophene	0.028
11	24.20	methyl-2-buthyldisulfide	0.057
Total concentration			0.529

The sulphur chemicals are thought to be the odour-generating compounds. The noteworthy fact is that among them only two types of disulfides can be distinguished. Kosmider et al performing their research based on the phosphoric acid manufacturing plant demonstrated that the most significant group of compounds containing sulphur was exactly disulfides [4]. These differences can result from distinct profile of phosphoric acid and superphosphate manufacturing processes, where only the reaction between sulphuric acid and phosphate rock is common. It is possible that odours can be generated during further stages of phosphoric acid manufacturing. The discrepancies in

composition of exhaust gases can result also from using different types of phosphate rocks. The particular phosphate rock is composed from wide spectrum of organic compounds, which quantity and concentration depends on place and period of rock formation [1].

Westerilch et al and Blazy et al did not reveal the presence of the compounds listed above in the organic phase during analysis of the phosphate rocks. It gives evidence that the thesis advanced by Westerilch et al concerning the generation of odours during reaction between sulphuric acid and phosphate rock is right. Therefore, apparatuses or even entire installations absorbing or neutralizing odour generating substances should be located on the outlet of the gas pipeline carrying gasses from the reactor [8, 9].

Finally on account of data deficiency in available references the comprehensive research regarding organic compounds in simple superphosphate manufacturing was suggested. The analysis of organic phase in phosphate rock and the subsequent analysis of exhaust gases during fertilizer manufacturing from previously investigated phosphate rock should be carried out. Determination of organic compounds concentration in ready product should constitute the successive step. The comprehensive investigations mentioned above could be very helpful with assessing the influence of phosphate rock organic phase components on odours formation in distinct stages of fertilizer manufacturing process. The results were also interesting for the people occupying with methods for deodorization of odours in phosphate industry, giving the opportunity for raising new approach to related problems. It could be chance for developing new solutions for improvement of odours neutralizing techniques in the phosphate rock-applied industry.

From the phosphate rocks yield and use forecast, results that on account of increasing demand for food in next several decades we can expect increased production of phosphate fertilizers. The renewable methods of gaining phosphates are not cost-effective yet in comparison with extracting. Due to this fact, in near future the emission of odour-generating substances will increase together with superphosphate manufacturing. It demonstrates how relevant works on law regulations and deodorization in this range are. In this elaboration the common discrepancies concerning comprehensive approach to identification of odour-generating compounds in phosphate rock-applied industry as well as neutralization of their presence in atmosphere were presented. The possible solutions for this problem were also suggested. Taking into consideration all factors mentioned above it can be stated that range of odour nuisance problems are essential for every developing society and require fast and efficient regulations.

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Abstrakt: W polskim ustawodawstwie istnieje bardzo dotkliwa dla obywateli i przedsiębiorców luka dotycząca regulacji prawnych związanych z uciążliwością zapachową. Po przeprowadzeniu analizy publikowanych projektów aktów prawnych i literatury z tego zakresu stwierdzono, że „ustawa odorowa” w proponowanym przez administrację państwową kształcie nie może wejść w życie. Jako przykład gałęzi przemysłu będącej przyczyną powstawania uciążliwości zapachowej wybrano procesy produkcyjne wykorzystujące surowce fosforanowe ze szczególnym uwzględnieniem produkcji superfosfatu prostego. W celu scharakteryzowania problemu dokonano analizy doniesień literaturowych dotyczących diagnozy i składu fosforytów pod kątem obecnej w nich fazy organicznej, z której w czasie produkcji nawozu powstają odoranty. W celu określenia obecności konkretnych związków odorotwórczych pobrano próbki gazów wylotowych z instalacji produkującej superfosfat prosty. Próbkę tę zanalizowano metodą TD-GC/MS pod kątem identyfikacji lotnych związków organicznych. Zidentyfikowano ponad 80 różnych związków a wśród nich: dużo alkanów, cykloalkanów, aromatów i organicznych związków siarki. Najprawdopodobniej za złoconość gazów wylotowych w największym stopniu odpowiedzialne są właśnie związki siarki. Ze względu na znikome informacje dotyczące właściwości złoconych mieszanin różnych związków nie można wykluczyć wpływu innych składników na zapach analizowanych gazów wylotowych. Ostatecznie ze względu na brak danych w dostępnej literaturze zaproponowano przeprowadzenie kompleksowych badań dotyczących związków organicznych w produkcji superfosfatu prostego. Z prognoz dotyczących wykorzystywania surowców fosforowych wynika, że w ciągu następnych kilku dekad czeka nas wzrost produkcji m.in. nawozów fosforowych. Dlatego należy jak najszybciej uporać się z problematyką uciążliwości zapachowej.

Słowa kluczowe: odory, superfosfat, lotne związki organiczne