Factors influencing the accuracy of content determination of chlorine in biofuels and solid recovered fuels

Monika BERDA, Leokadia RÓG – Central Mining Institute, Department of Solid Fuels Quality Assessment, Katowice, Poland

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Introduction

Chlorine, as well as nitrogen and sulphur, is an element occurring in diverse quantities both in solid biofuels and solid recovered fuels. Chlorine occurrence in those fuels may have harmful effects on the environment and for the system, in which solid biofuels and solid recovered fuels are used in the process of combustion or co-combustion. In the process of pyrolysis and combustion the impact of the temperature on the solid fuels results in liberation of chlorine contained in the fuels in the form of different compounds. Some of them move into gas phase causing development of, among others chloride, which is a compound aggressive for electrical equipment (leading to corrosion of construction elements of combustion equipment, and development of deposits on the heating surfaces). Moreover, chlorine is an agent acidifying environment (as well as forming organochlorine compounds, highly harmful for the living organisms). Other compounds move to solid products forming in the combustion process (slag and ashes), causing a change in the properties of these products in the scope of fusibility and occurrence of seizing and fouling of heating elements of the furnace. Co-combustion of coal and solid biofuels or solid recovered fuels may lead to intensification of those negative occurrences.

The way chlorine compounds occur in solid biofuels or solid recovered fuels was, and still is, an essential and not explicitly explained research problem. It is caused by complex chemical structure of solid fuels. Used methods for chlorine determination are based on its release from solid fuels in physical or chemical processes, so through elution or heating the sample. Other compounds are released in such conditions of those negative occurrences.

Solid biofuels utilization in the energetics

Solid biofuels, categorized as recovered energy sources, are produced in natural biological processes and contain coal and hydrogen as energetic elements. Solid biofuels are also decomposition products from agriculture, both plant and animal, forestry and related industries, including industrial and agricultural waste. Wide interest in solid biofuels production results from the following [1]:

• renewability of resources
• zero balance circulation of carbon dioxide in nature and substantial limitation of harmful substances emission into the atmosphere
• activation of economic rural areas aimed at reduction of unemployment in such areas
• productive use of land set aside or not suitable for food production.

In August 2004, the Chairman of the Regulatory Office (ERO), granted the first license to produce electricity and heat through joint combustion of solid biofuels (wood chips) and fossil fuel (coal). Since then, significant progress has been noted in the development of this technology, both in terms of experience of operation in Poland, as well as in the standardization processes carried out by the European Committee for Standardization [2].

When evaluating solid biofuels in terms of energy, the same rules apply as in the evaluation of traditional solid fuels. When comparing the energy properties of coal and solid biofuels, it was found that quality of basic elemental composition is the same, but differences exist in quantitative composition [3]. Biofuel based on wood contains about four times more oxygen, twice less carbon and much less sulfur and nitrogen. It also contains lower, in comparison with coal, quantity of ash and chlorine. Indisputable advantage of solid biofuels is the zero balance of carbon emissions during the combustion process. An unfavorable feature of solid biofuels however, is high and variable moisture content, depending on the type and duration of storage and results in a low calorific value. In comparison with coal, solid biofuels are characterized by much higher content of alkali metal compounds (particularly potassium hydroxide), calcium and phosphorus, which can lead to increased corrosion and corrosive sludge accumulation in the furnace during combustion. Significant difference is the much lower bulk density of solid biofuels, which requires more storage space and more efficient traffic flow [3].

Utilization of solid recovered fuels in energetics

Despite the fact that significant part of solid recovered fuels has advantages in terms of energy, their use for the production of electricity and heat in Poland is scarce. The reason for this is the number of obstacles, both of a technical and formal – legal nature, which must be faced by an energy producer intending to implement an energy recovery of waste. Furthermore, an additional complication is that the solid recovered fuels are generally characterized by significant heterogeneity, which is the cause of lack of stability in the quality parameters during the utilization [4].

However, strong reasons for using solid recovered fuels in the power industry are [5]:

• potential increase in the amount of produced electricity from recovered sources
• reduction in reported CO₂ emissions in the energy sector (savings of CO₂ emission limits allocated to the sector)
• increase in the level waste recovery (meeting the recommendations of the EU waste management)
• increase in revenues of energy producers due to lower fuel price produced from waste in comparison with fossil fuels.

Solid recovered fuels can be produced from waste other than hazardous. A classification system for solid recovered fuels proposed by the European Committee for Standardization is based on three key parameters determining the properties of these fuels [4]:

• caloric value
• chlorine content
• mercury content.

The choice of these parameters takes into consideration three aspects of the fuel assessment, associated with its economic, technological and emission use. Five quality classes were designed for each of the three parameters describing the solid recovered fuels, specifying limit values for each of the classes. The combination of the numbers of classes, results in classification code of fuel.
Methods for determination of chlorine content in solid biofuels and solid recovered fuels

Commonly applied method for determining chlorine in solid fuels is the method based on Eschka mixture. This is a standardized method, designed for hard coal, brown coal ( lignite) and the coke, as described in the polish standard ISO 587:2000. [6] It presents three methods for determining chlorine content in solid fuels. The first method is the Volhard method, the second is the Mohr method, and the third is the method of potentiometric titration using an ion-selective electrode. In each of these methods, a sample of known mass, this is in direct contact with the Eschka’s mixture, burns at an oxidizing atmosphere to remove the combustible substance and forming alkali chlorides from chlorine. Formed chlorides are extracted with nitric acid (V) or with water, and are determined by the Volhard or Mohr method, or by potentiometric titration using ion-selective electrode (ISE) [6].

Currently, in connection with launching of a new automatic analyzer multi EA 4000 produced by a German company Analytikjena, a modern method of determination of chlorine content has appeared, based on coulometric analysis, which is not yet standardized method.

The principle of operation of the analyzer is based on coulometric analysis after the thermal decomposition of the sample takes place in the quartz tube. The sample that is to be tested is inserted into the combustion chamber in a quartz boat through the open inlet gas. Analysis of temperature can take place in two ways, depending on the type of sample. One possibility is the direct combustion in an oxygen stream. The second option is the pyrolysis of the sample in a stream of inert gas (argon) at a temperature of between 300°C and 600°C, in the front part of the furnace, and the pyrolysis products are completely combusted with a slight delay in an oxygen stream, in the rear part of the furnace, at 1100°C. The latter method is recommended for organic substances that can burn explosively in an aerobic environment.

These reactions are described by the equation (1):

\[ R - Cl + HCl \rightarrow CO_2 + H_2O + oxides \] (1)

HCl is determined by coulometric analysis, after drying the gas to be analyzed (with sulfuric acid). Chlorine ions react completely with silver ions, deriving by electrolysis and silver chloride is obtained, as according to equation (2) and (3).

\[ Ag^+ + Cl^{-} \rightarrow AgCl \] (2)

\[ Ag^+ + e^{-} \rightarrow Ag \] (3)

The quantity of chlorine from required charge to produce silver ions can be calculated using Faraday's law [7]. The entire analytical cycle, conducted using an automated analyzer is operated by a computer, from the moment of acceptable weighing of the test sample to obtaining the results in printed form.

The basic advantages of the analyzer include:

• short analysis time: about 15 minutes
• high sensitivity and accuracy of the analysis
• positional input tray (auto sampler) for simultaneously 48 samples (analysis), an automatic sample input to the furnace with flame sensor that determines the speed of combustion of the samples which minimizes smudges of dirt of combustion pipes
• easy-to-use MultiWin software, enabling graphic visualization of the determination process
• low cost of operation of the device and low reagent consumption (about 120 ml of electrolyte, and about 15 ml of concentrated H2SO4 for one run of the analyzer)
• depending on the sample matrix and expected concentration, the analysis can be performed with distribution of gas to be analyzed (at high concentrations of chlorine), or without separation of the gas (at low concentrations of chlorine). When the unit is working with gas distribution, gas to be analyzed is divided into a predetermined proportional basis and coulometric cell receives only a certain amount of gas to the reaction.

Previous experimental studies concluded that:

• for all samples of solid recovered fuels, the method should be used with 20% of the gas distribution (split ratio 1/5), as in the method without the gas distribution the analysis is not completed (solid recovered fuels contain too high concentrations of chlorine)
• for certain types of solid biofuels, such as olive oil or oil cake, the method without gas distribution cannot be use, since combustion of samples in a quartz tube is too violent and it leads to the “explosion” of the sample (termination of the analysis). Even covering samples with sea sand does not give positive results of the analysis. In such cases it is necessary to change the method of analysis of 20% of the gas distribution
• high concentrations of chlorine and poorly matched sample masses for testing cause that the analysis is not complete, meaning that it reaches the final cut-off point (so-called „end point rutine”) in which the system turns off. This leads to the need to replace the electrolyte due to too high amount of chlorine ions in the coulometric cell
• heterogeneity of solid recovered fuels causes major discrepancy between the results
• sample weight used to analyze the determination of chlorine in solid recovered fuels, should be about 100 mg (greater sample weight causes that the analysis does not end, which leads to distortion of the results)
• milled samples below 3 mm, show minor homogeneity (during sample grinding to a grain size below 3 mm occurs deposition of the bigger components of the sample in the cylinder of the grinding device, which then do not reach the sample to be tested).

A standardized method was used to determine the amount of chlorine in the solid biofuels and solid recovered fuels for the purposes of this publication. The method uses the Eschka mixture, so called Volhard method (due to the long experience of the Department of Solid Fuels Quality Assessment in the determination of chlorine content by this method) and a method based on coulometric analysis, using an automatic analyzer.

The test procedure

The objects of the study were three samples of solid biofuels, and three samples of solid recovered fuels, with different chlorine content. In order to determine the factors affecting the accuracy of determination of chlorine content in the samples of solid biofuels and solid recovered fuels, and to develop reliable methods for the determination of chlorine in these fuels were used various types of fuel, various methods for the determination, samples of different particle size and different weight (sample weight) of samples.

Graphic representation of the process and the solid biofuel sample during the research implementation is shown in Figure 1. Graphic representation of the process and the solid recovered fuel sample during the research implementation is shown in Figure 2.

![Fig. 1. Procedure of the solid biofuel sample during the tests](image-url)
The subjects of the study were:

- samples of different types of solid biofuels (i.e., wood chips, straw briquettes and wood pellets), obtained in energy plants that carry co-combustion of solid biofuels and coal. Obtained samples prior to grinding, were dried to air-dry state, by spreading them in a thin layer on a plastic tray. After drying, all samples were fragmented using a laboratory knife mill produced by “TestChem” and a laboratory cryogenic mill produced by SPEX SamplePrep. As a result of grinding, following grain size samples were obtained: <3 mm <1 mm <0.5 mm (ground in a knife mill), as well as of grain size, which was created after grinding in the cryogenic mill

- samples of solid recovered fuels, obtained as a result of the cooperation with three departments dealing with waste management. Obtained samples prior to grinding, were dried to air-dry state, by spreading them in a thin layer on a plastic tray. After drying, all samples were fragmented using a laboratory knife mill produced by „TestChem” and a laboratory cryogenic mill produced by SPEX SamplePrep. As a result of grinding, following grain size samples were obtained <3 mm <1 mm <0.5 mm (ground in a knife mill), as well as of grain size, which was created after grinding in a cryogenic mill. Fragmentation test was performed at the same time of solid recovered fuel samples; grain size <1 mm and <0.5 mm, using a laboratory knife mill. The problem that emerged during grinding to a grain size <1 mm and <0.5 mm in the knife mill, is the separation and deposition in the cutting chamber of the mill of plastic, among other materials with high content of chlorine resulting in a low effectiveness of grinding fractions, and samples of such grain sizes were removed from the research.

Chlorine determination for each sample of solid biofuel and solid recovered fuel was made by both methods.

### Test results

Own research were used to identify factors affecting the accuracy of the determination of the chlorine in biofuels and solid recovered fuels. Following aspects were taken into account during the comparative analysis of the results of the study:

- different research methods
- variety of tested fuels
- different granulation of testes samples
- different sample weights used during the analysis.

Test results are shown in Tables 1 and 2.

Graphic representation of the analysis of chlorine determination, using a method based on coulometric analysis and using an automatic analyzer, for selected samples is illustrated in Figures 3÷8.
Table 2
Results of the determination of chlorine in samples of solid recovered fuels

<table>
<thead>
<tr>
<th>Determination of chlorine [%]</th>
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<tbody>
<tr>
<td>Sample mass</td>
<td>Sample mass</td>
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<tr>
<td>50 mg</td>
<td>100 mg</td>
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<tr>
<td>200 mg</td>
<td>500 mg</td>
</tr>
<tr>
<td>900 mg</td>
<td>2.000 g</td>
</tr>
<tr>
<td>5.000 g</td>
<td>10.000 g</td>
</tr>
</tbody>
</table>

| MB13/12 SRF Firma X 3 mm     | 1.070 1.310 2.190 0.638 0.896 0.737 0.743 |
| MB16/12 SRF Firma X cryogenic mill | 2.700 2.030 1.840 1.550 1.170 1.135 0.907 0.915 |
| MB17/12 SRF Firma Y 3 mm     | 0.468 0.764 1.090 1.150 0.476 0.421 0.398 |
| MB20/12 SRF Firma Y cryogenic mill | 1.150 1.480 1.370 1.070 0.840 0.788 0.666 |
| MB21/12 SRF Firma Z 3 mm     | 0.470 1.090 1.920 0.897 0.896 0.638 0.059 |
| MB24/12 SRF Firma Z cryogenic mill | 1.630 1.730 1.600 1.530 0.740 0.609 0.208 |

Fig. 3. Graphic representation of the analysis of chlorine content determination for a wood chips sample, grain size 3 mm (sample mass: about 50 mg)

Fig. 4. Graphic representation of the analysis of chlorine content determination for a wood chips sample, grain size 3 mm (sample mass: about 500 mg)

Fig. 5. Graphic representation of the analysis of chlorine content determination for a wood chips sample, grain size 1 mm (sample mass: about 100 mg)

Fig. 6. Graphic representation of the analysis of chlorine content determination for a straw briquette sample, grain size 3 mm (sample mass: about 900 mg)

Fig. 7. Graphic representation of the analysis of chlorine content determination for a sample of solid recovered fuel, fragmented in cryogenic mill (sample mass: about 100 mg)

Fig. 8. Graphic representation of the analysis of chlorine content determination for a sample of solid recovered fuel, fragmented in cryogenic mill (sample mass: about 500 mg)
While comparing the method for determining chlorine content using an automatic analyzer (so-called coulometric method), with the Volhard method, i.e. by using Eschka mixture, were noted differences in the obtained result, both during analysis of solid biofuels samples and samples of solid recovered fuels. Thorough analysis of the results indicates that in the majority of samples of solid biofuels and solid recovered fuels (for example, based on the results of tests for the sample weight of 0.5 g), the chlorine content determined by the Volhard method, using the Eschka mixture, is lower than the amount of chlorine determined by the coulometry method. The handling of the sample during testing was traced in order to explain the reasons for discrepancies in the achieved results of chlorine content determination by the two methods. Scheme of sample handling is shown in Figure 9 [8].

![Fig. 9. Scheme of sample handling during the determination of the chlorine content by coulometry and by the Volhard method](image)

The above scheme of workflow of the sample during the determination of the chlorine content shows that in the Volhard method, using the Eschka mixture, only chloride ions Cl\(^-\) extracted from the fuel sample with nitric acid (the organic part of the sample) are noted, while, in the coulometric analysis, using an automatic analyzer, a sample of fuel is combusted at a temperature of about 1 100°C and the resulting gas contains chlorine (as HCl) from all the compounds (organic and inorganic) present in solid biofuels and solid recovered fuels. [8] On this basis, it can be concluded that Coulometric method is more accurate.

The Volhard method is very subjective and not very accurate. It is a typical chemical method in which a research result depends upon various factors, such as quality of chemical reagents, environmental conditions and precision of executive personnel. In addition, the Volhard method is very time-consuming. The average time of the determination of chlorine content by the Volhard method is about 6.5÷7 hours (in comparison with the automatic analyzer, which analyzes a sample for about 15 minutes).

Differences between the various results may be noticed after performing determinations of chlorine content for three samples of solid biofuel and three samples of solid recovered fuel using different grinding samples. This is due to the heterogeneity of the analytical samples, resulting from different degrees of fragmentation, especially in the case of solid recovered fuels, where the result of the determination of chlorine in samples milled in a cryogenic mill is generally higher from the result of determination of the samples with a particle size of less than 3 mm, milled in a knife mill.

Comparing the results of analysis of samples obtained for ground samples <3 mm, <1 mm, <0.5 mm and those fragmented in a cryogenic mill, a conclusion was formulated that the best reproducibility of the results were obtained for samples of solid biofuels, fragmented using a cryogenic mill, in which even the use of a different analysis of the sample did not affect the final result. The deeper the fragmentations of the samples, the differences between the results are smaller. Only in the case of certain types of solid recovered fuels, the differences are greater, even in the case of a cryogenic fragmentation mill. The reason for this is high heterogeneity of these fuels and lack of ability to complete fragmentation of the sample (some elements of the sample during milling, are deposited on the walls of the cutting mill, which leads to classification of the samples). Therefore, the accurate "depth" of sample fragmentation obtained by a cryogenic mill contributed to improving their uniformity and higher reproducibility of the results.

Simultaneously, the influence of the size of the test portion on the determination of chlorine was observed during the test. Following conclusion arised from the observations:

- the result obtained using the sample test portion of approximately 500 mg is the most reliable for samples of solid biofuels (Fig. 4). With weight of the sample, the analysis occurs slowly, does not cause pollution of the sulfuric acid and the various parts of the analyzer, and it ends at a certain time. Too small amount of the test sample of 50 mg, 100 mg or 200 mg (Fig. 3, Fig. 5), causes that the analysis (reaction) does not occur (the diagram from the analysis has no regular shape), leaving the low unburned sample particles on the combustion boat, and the result of determination is 0% (in the case of a sample of wood chips, grain size <3 mm and <1 mm). However, too many test sample of 900 mg (Fig. 6) cause high pollution of the analyzer (sulfuric acid, which acts as a gas dryer becomes black, and the combustion tube and the cables of the analyzer contaminate in an irreversible way) and air pollution around the analyzer (fumes characterized by intense, unpleasant odor are let out from combustion pipes). The analysis is not completed within the specified time, so that the result is distorted (as seen in Fig. 6 and Fig. 8). Therefore, the tests for samples from MB1/12 to MB8/12 were not performed with sample mass of 900 mg
- the result obtained using the sample test portion of approximately 100 mg, but not more than 200 mg is the most reliable for samples of solid recovered fuels (Fig. 7). Too large amount of the test sample, greater than 200 mg (Fig. 8) may cause that the analysis will not be completed within the specified time, giving unreliable results of the examination, while the use of 900 mg of the test portion is often not possible, since such samples does not fit in the combustion boat. Only 900 mg of the sample ground in a cryogenic mill sometimes fit in a crucible, but also such sample does not provide the final determination result (analysis does not end)

In conclusion, it is recommended that the determination of chlorine in solid biofuels and solid recovered fuels is performed using the method based on coulometric analysis on samples fragmented by cryogenic mill, assuming a test sample of:

- solid biofuels samples of about 500 mg
- solid recovered fuels samples of about 100 mg, but not more than 200 mg.

**Conclusion**

- The method based on the Eschka mixture (the Volhard, Mohr or potentiometric titration method) was previously used for the determination of chlorine content in the solid fuels. A new possibility for determining of chlorine content and also alternative analytical technique is a method based on coulometric analysis, using an automatic analyzer 4000 Multi EA. This method allows the determination of chlorine content in, among others, solid biofuels and solid recovered fuels in a wide measuring range
- Some differences in the results of chlorine content achieved by Volhard method and the method based on coulometric analysis were noted in samples of biofuels and solid recovered fuels based on the results from research. Therefore, two methods for the determination of chlorine should be considered separately, but a more accurate method is coulometric analysis because the sample of fuel is combusted at a temperature of about 1 100°C, and the resulting gas contains chlorine (as HCl) from all compounds (organic and inorganic) present in the solid biofuels and solid recovered fuels [8]
• The occurrence of discrepancies between the results were noted based on the results of the determinations of samples of solid biofuels and solid fuels recovered fragmentation using different samples. This is due to the heterogeneity of test samples, obtained as a result of varying degrees of fragmentation. Fragmentation of the sample to a grain size below 3 mm for solid samples recovered fuels, unable to produce reliable tests for the presence of chlorine, because of classification of the samples, mainly plastics with high chlorine content, which often do not reach a to the portion of the sample subjected to testing. The deeper the fragmentation of the samples, the differences between the results are smaller. The usage of a cryogenic mill to ground the samples contributes to improving their uniformity and higher reproducibility of the results.

• It is recommended to determine chlorine content in solid biofuels and solid recovered fuels using the method based on coulometric analysis on samples fragmented by cryogenic mill, assuming a test sample of:
  - for solid biofuels samples of about 500 mg
  - for solid recovered fuels samples of about 100 mg, but not more than 200 mg.

• The knowledge of the chlorine becomes more complete through the use of modern methods of coulometric, designed to determine chlorine content in fuels, such as in the solid biofuels and solid recovered fuels.

Literature


Translation into English by the Author

Monika BERDA – M.Sc., is a graduate of the Faculty of Mathematics, Physics and Chemistry at the University of Silesia (2005), with a specialization in environmental chemistry. She has been working in The Central Mining Institute in Katowice since 2005, first as an employee of the Department of Solid Fuels Quality Assessment, and from 2010 as Deputy Head of the Department. Moreover, she is also an internal auditor in the laboratory and the examiner in the Certification Body of the Central Mining Institute. During her professional career she has completed numerous trainings and courses on: operation of equipment, systems and network at operating position, sampling of current technical standards PN and ISO, management systems in laboratories, measurement uncertainty estimation, test methods used to evaluate the quality of solid fuels. She is the author of 3 statutory works and co-author of 1 statutory and 1 publication as well as the author of numerous implemented researches – development works. Research interests: solid fuel, sampling, chlorine content in fuels.

e-mail address: m.berda@gig.eu, phone: +48 32 259 22 41

Leokadia RÓG – Ph.D., Head of Department of Solid Fuels Quality Assessment in the Central Mining Institute, Katowice. Leokadia Róg graduated from the Faculty of Earth Sciences, University of Silesia faculty of geology. She defended her doctoral dissertation in chemical engineering at Wrocław University of Technology. In addition, she completed postgraduate studies in Applied Statistics at the Faculty of Mathematics and Physics of the Silesian University of Technology in 2010. Leokadia Róg has been working in The Central Mining Institute in Katowice since 1984, at first as an employee of the Applied Petrography Laboratory in the Department of Mining Geology, between 1991 – 2000 as Deputy Head of Coal Quality Assessment and Forecast Laboratory, and since 2000 as she has worked Head of the Department of Solid Fuels Quality Assessment. During her professional career she has completed numerous professional training courses related to: management systems according to the ISO standards, process management, and human resources, adaptation of the Polish standards to the European Union requirements, the rules of the Polish standardization of test methods used to evaluate the quality of fuels. The key experience includes the cooperation with producers and users of solid fuels, understood in a broad sense, including the current trends of biofuels and solid secondary fuels. One of the main activities is the recognition of the impact of fuel quality on the technological processes with the ability to optimize the fuel selection for specific applications, classification of coals from the point of view of the degree of coalification of organic carbon and classification technology. An important element of the research is the analysis of the influence of petrographic composition of coals on their technological properties. The results of this activity are numerous research publications in the national and international journals. An important experience is work for the: Committee of the Polish Academy of Sciences Mining Mineral Resources Section, Polish Society of Mineral, Coal Petrology Section of the Polish Geological Society, Standardization Technical Committees No. 220 on Natural Solid Fuels (Chair) and 144 for Coke and solid Fuels Processed (member). Member of the Sectoral Council, Polish Mining Sector of Standardization Committee.

e-mail address: l.reg@gig.eu,
phone: +48 32 259 22 76, +48 512 293 854

Nowy plastylifikator Grupy Azoty

W 2015 r. Grupa Azoty Zakłady Azotowe Kędzierzyn SA uruchomiła linię do produkcji nowego plastylifikatora, alternatywnego dla ftalanu dwuoktylu (Oxoplast O), który coraz częściej – choć na razie bez konkretnych podstaw – uważany jest za substancję niebezpieczną dla zdrowia. Koszt budowy instalacji wyniesie kilka-dziesiąt mln PLN. Jej wydajność ma sięgać 50 tys. ton plastylifikatora Oxoplast OT rocznie. Co ciekawe, niechciany ftalan dwuoktylu jest jednym plastylifikatem zaakceptowanym do stosowania w przemyśle medycznym, m.in. do produkcji sprzętu medycznego. (kk)

(http://eplastics.pl, 3.09.2013)