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# CORROSIVE PROPERTIES OF LPG AND PROBLEMS WITH THEIR DETERMINATION

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## Summary

The corrosiveness of gaseous fuels is a known and frequently encountered problem, but the methods employed to explore this issue not always lead to the obtaining of reliable results. This article presents results of interlaboratory comparisons carried out to verify the method of evaluation of the corrosiveness of liquefied petroleum gas (LPG) according to Standard PN-EN ISO 6251. The corrosiveness of LPG to copper was tested for four different samples of the LPG fuel.

**Keywords:** LPG, copper corrosion, degree of corrosion

## 1. Introduction

The liquefied hydrocarbon gas, referred to as LPG (liquefied petroleum gas), is the Poland's most popular alternative fuel [3]. Both in the production process and during transport, this fuel is exposed to the impact of many unfavourable factors. The LPG quality is particularly jeopardized during the transshipment processes in transport, when this fuel may be exposed to the penetration of such substances as water and sulphur compounds into it. The contaminants present in LPG may cause corrosion of the structural materials being in contact with this fuel, e.g. fuel system components, gasholders, or transmission installations. The solid products of corrosion processes are mechanical contaminants, which, having penetrated with the fuel into the gas feeding system of a vehicle, may cause damage to system components [1, 6].

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The LPG chiefly consists of alkanes (having three or four carbon atoms in a molecule), alkenes, or is a mixture of both. These LPG components do not cause corrosion. In most cases, corrosion changes are caused by sulphur compounds such as  $H_2S$  (hydrogen sulphide) occurring in LPG in trace amounts, mercaptans, COS (carbonyl sulphide), elemental sulphur (in the form of eight-atom cyclic molecules,  $S_8$ ), and atmospheric water and oxygen [1, 3, 6, 8]. The corrosion of various metals goes in different ways, depending on the type of the chemical compound in which sulphur is contained. As an example, the copper corrosion caused by elemental sulphur goes 3.7 times faster than the corrosion caused by ethyl mercaptan (ethanethiol) [2]. Hydrogen sulphide ( $H_2S$ ), which may originate from production processes, has corrosive properties, especially in the presence of water. Experiments carried out have shown that the presence of hydrogen sulphide in LPG, in as low a concentration as 5 ppm, causes changes in the test copper strip in the form of multicolour green-pink-purple corrosion products, chiefly consisting of copper(I) sulphide and copper(II) sulphide. The hydrogen sulphide present in LPG may also be oxidized to elemental sulphur ( $S_8$ ) [8]. In this case, at as low a concentration of  $S_8$  as 5 ppm, black copper(II) sulphide tarnish is formed on the copper strip surface. The situation is different in the case of carbonyl sulphide (COS), which does not cause corrosion of test copper strips even at concentrations of up to 100 ppm, but in the presence of water, it hydrolyses to  $H_2S$  and  $CO_2$ , which may accelerate the corrosion processes. Carbon dioxide in the concentration range of 10-1 000 ppm in LPG does not contribute to the formation of corrosion changes, either, but at higher concentrations, changes in the copper colour to greenish can be observed. Interestingly, the mixture of sulphur compounds present in LPG is more corrosive than each of the compounds acting separately, even if the concentration of the compound involved acting alone is higher [6, 8].

Inspections carried out by Państwowa Inspekcja Handlowa (National Trading Standards Authority) to commission of Urząd Ochrony Konkurencji i Konsumentów (Office for Competition and Consumer Protection) revealed in 2015 an increase in the number of the filling stations where shortcomings were detected in the quality of the LPG being sold there. The exceedances were detected in two parameters, i.e. sulphur content and exactly the corrosiveness of LPG to copper [7]. The corrosiveness of gaseous fuels is a known and frequently encountered problem. However, the determination of the corrosive impact of LPG is not always easy and unequivocal, which has been confirmed by results of inter-laboratory comparisons organized by the Automotive Industry Institute (PIMOT). The inter-laboratory comparisons have the form of research where at least two laboratories carry out tests and assessment of identical objects (samples) in accordance with a predefined procedure and test conditions [4]. The research presented herein was undertaken to compare the results of tests carried out by the laboratories involved and to verify the usability of the method of determining the corrosiveness of LPG to copper according to Standard PN-EN ISO 6251 [5].

## 2. Materials and test methods

The interlaboratory comparisons were carried out in compliance with the requirements of Standard ISO 17043. The comparative LPG tests were carried out with participation

of eight laboratories. Each laboratory received four LPG samples (LPG/01, LPG/02, LPG/03, and LPG/04) for testing. The chemical composition of individual samples has been presented in Table 1 and selected physicochemical characteristics of the samples have been brought together in Table 2. The LPG batches were so selected that they were characterized by different corrosion classes. Each test sample was taken to a new gas cylinder of 11 kg capacity, made of acid-resistant steel meeting the requirements of Standard PN-EN ISO 4257:2004.

The test samples were taken in the second half of April and the required test completion time was set for the laboratories to the first half of May. According to the requirements laid down for the interlaboratory comparisons of the LPG batches under test, the homogeneity and stability of the samples was tested and the test results confirmed that individual laboratories had received samples of identical test material.

Table 1. Chemical composition of the LPG samples

Component [% m/m]	Sample			
	LPG/01	LPG/02	LPG/03	LPG/04
Methane	<0.1	<0.1	<0.1	<0.1
Ethane	1.59	0.11	1.07	1.12
Ethene	<0.1	<0.1	<0.1	<0.1
Propane	44.93	12.73	49.67	47.73
Propene	1.03	34.53	6.41	3.9
n-Butane	24.49	9.22	17.69	20.42
Trans-2-butene	<0.1	6.5	0.96	0.57
Cis-2-butene	<0.1	4.36	0.66	0.4
i-butane	27.72	21.63	22.26	25.09
1-butene	<0.1	5.88	0.87	0.52
i-butene	<0.1	4.93	0.41	0.24
1,3-butadiene	<0.1	<0.1	<0.1	<0.1
1,2-butadiene	<0.1	<0.1	<0.1	<0.1
n-pentane	<0.1	<0.1	<0.1	<0.1
i-pentane	<0.1	<0.1	<0.1	<0.1

Individual LPG components were determined in compliance with the requirements of Standard PN-ISO 7941. This method is applicable to the determination of the LPG components whose contents exceed 0.1 % m/m. It may be employed at the analyses of propane, butane, and their commercial blends containing saturated and unsaturated hydrocarbons, ranging from the C<sub>2</sub> to C<sub>5</sub> types and including methane.

Table 2. Selected physicochemical characteristics of the samples under test

	Parameter determined	LPG/01	LPG/02	LPG/03	LPG/04
1	Motor octane number	94.3	86.9	93.4	93.8
2	Temperature at which the relative vapour pressure is not less than 150 kPa; fuel grade	-10 (grade A)	-10 (grade A)	-10 (grade A)	-10 (grade A)
3	Relative vapour pressure at 40 °C	971.7	982.8	1049.6	992.1
4	Copper strip corrosion test (1 h at 40 °C)	class 2	class 1	class 1	class 3

The motor octane number of a sample is calculated by summing up partial products of octane numbers of individual LPG components and the percentage concentrations of the respective components in the sample, determined from the analysis.

### 3. Evaluation of the corrosiveness of LPG to copper

The laboratories determined the corrosiveness of LPG to copper by carrying out copper strip corrosion tests in compliance with Standard PN-EN ISO 6251:2001 [5]. In this method, polished copper strips are immersed for 1 h in a 100 ml LPG sample saturated with water at a temperature of 40 °C, contained in a "test bomb" designed for the corrosion tests. Afterwards, the copper strip is removed from the bath and the corrosive action of the LPG sample on copper is assessed by comparing the strip with Copper Strip Corrosion Standards (Fig. 1) and by determining the corrosion class according to Table 3.

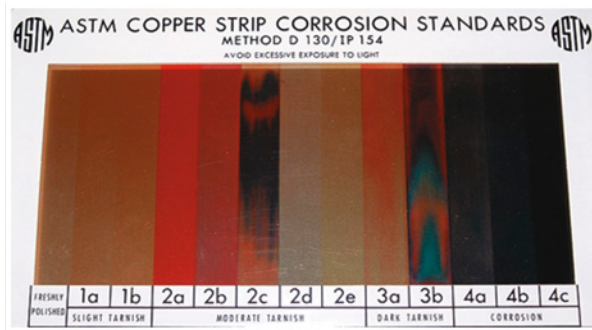


Fig. 1. Copper Strip Corrosion Standards quoted in Standard PN-EN ISO 6251, which may be taken as a reference for determining the degree of corrosion of a test copper strip

Table 3. Description of the degree of corrosion of a test copper strip, according to Standard PN-EN ISO 6251 [5]

Degree of corrosion	Qualifying term	Description
Strip freshly polished	No tarnish	
1	Slight tarnish	Light orange colour, almost identical to that of the strip freshly polished; Dark orange colour
2	Moderate tarnish	Claret-red colour; Light purple colour; Multicolour surface with purple-blue and/or silver tarnish against claret-red background; Silver colour; Brass- or gold-coloured surface
3	Dark tarnish	Purple tarnish against brass-coloured background; Multicolour surface with red and green (peacock blue, but not grey) spots
4	Corrosion	Black translucent, dark-grey, or brown colour with green (peacock blue) spots; Graphite-black or matt-black colour; Glossy black or raven-black colour

The corrosive impact of LPG is evaluated visually; admittedly, this is a subjective method. The result may be affected by e.g. method of preparing the copper strip for testing, contact of the copper strip with a wall of the test bomb, completeness of filling the bomb with the liquid phase of LPG, lighting type, angle of light incidence, as well as observer's colour recognition ability and experience in the carrying out of tests of this kind. The laboratories participating in the interlaboratory comparisons not only determined the copper strip corrosion class in compliance with the said Standard but also sent photographs that illustrated the copper strip surface state immediately after the test.

#### 4. Test results and discussion

Results of determining the corrosiveness of individual LPG samples by the laboratories have been brought together in Table 4. For the needs of the interlaboratory comparisons, a "reference result" is usually determined. For qualitative parameters, where no numerical figure is obtained as a measurement result, the textual expression that repeats in at least 70 % of the judgments is recognized as the reference result. Due to wide scatter in the results received from the laboratories participating in the interlaboratory comparisons, no reference result could be correctly determined in the case under consideration.

Table 4. Summary of the dates and results of determining the copper strip corrosion classes by the laboratories participating in the interlaboratory research

Sample LPG/01		Sample LPG/02		Sample LPG/03		Sample LPG/04	
<i>Date</i>	<i>Result (class)</i>	<i>Date</i>	<i>Result (class)</i>	<i>Date</i>	<i>Result (class)</i>	<i>Date</i>	<i>Result (class)</i>
22 April	2	22 April	1	22 April	4	22 April	3
23 April	4	23 April	2	23 April	1	23 April	3
26 April	2	26 April	3	26 April	4	26 April	2
28 April	4	28 April	2	28 April	1	28 April	3
06 May	4	06 May	4	06 May	1	06 May	4
10 May	1	09 May	1	10 May	3	09 May	1
13 May	2	10 May	2	13 May	2	10 May	2
14 May	2	13 May	1	13 May	2	13 May	1

For all the LPG samples under test, the results obtained were widely scattered.

For sample LPG/01, the copper strip corrosion was reported to be of class 1 by only one laboratory, which makes 12.5 % of all the results obtained. Corrosion class 2 was reported by four laboratories, which made 50 % of all the results. The corrosive impact of this LPG sample was qualified for class 4 by three laboratories (37.5 % of the total). These results are confirmed by the photographs sent by the laboratories to illustrate the copper strip surface state after the corrosion test (Table 5).

For sample LPG/02, copper strip corrosion classes 1 and 2 were reported by 37.5 % of the laboratories in each case, and the remaining laboratories qualified the corrosion for classes 3 and 4 (12.5 % of the laboratories in each case).

The look of the test copper strips exposed to the impact of sample LPG/02 and the corrosion evaluation results reported by the laboratories have been presented in Table 6.

For sample LPG/03, three laboratories qualified the corrosion changes observed on the copper surface for class 1, which indicates low corrosive impact of LPG. In this case, the participants in the interlaboratory research only observed slight tarnish on the test copper strips. Interestingly, two other laboratories examining samples taken from the same LPG batch observed dark-grey tarnish spots on the surfaces of the test copper strips, which qualified the corrosion for as high a class as 4 (Table 7).

In the case of sample LPG/04, most of the laboratories, whose findings made 37.5 % of all the relevant test results, recognized the changes observed on the copper surface as changes corresponding to corrosion class 3 (Table 8). The other participants qualified the effects of the corrosive attack of this LPG sample for class 2 (two laboratories, i.e. 25 % of all the test results), for class 1 (another two laboratories, i.e. again 25 % of all the test results), and for class 4 (one laboratory, i.e. 12.5 % of all the test results).

Table 5. Photographs showing the corrosion classes determined for copper strips exposed to the impact of sample LPG/01









Laboratory code	LAB 1	LAB 2	LAB 3	LAB 4	LAB 5	LAB 6	LAB 7	LAB 8
Photograph								
Laboratory's finding	Class 1	Class 2e	Class 4	Class 2	Class 2	Class 4	Class 2	Class 4

Table 6. Photographs showing the corrosion classes determined for copper strips exposed to the impact of sample LPG/02



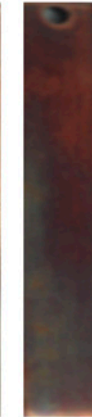


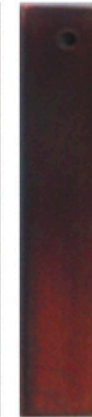


Laboratory code	LAB 1	LAB 2	LAB 3	LAB 4	LAB 5	LAB 6	LAB 7	LAB 8
Photograph								
Laboratory's finding	Class 2	Class 3a	Class 2	Class 1	Class 1	Class 2	Class 1	Class 4

Table 7. Photographs showing the corrosion classes determined for copper strips exposed to the impact of sample LPG/03















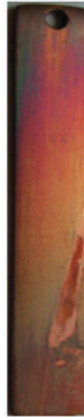

Laboratory code	LAB 1	LAB 2	LAB 3	LAB 4	LAB 5	LAB 6	LAB 7	LAB 8
Photograph								
Laboratory's finding	Class 3	Class 4a	Class 1	Class 2	Class 2	Class 1	Class 4	Class 1

Table 8. Photographs showing the corrosion classes determined for copper strips exposed to the impact of sample LPG/04

Laboratory code	LAB 1	LAB 2	LAB 3	LAB 4	LAB 5	LAB 6	LAB 7	LAB 8
Photograph								
Laboratory's finding	Class 2	Class 2c	Class 3	Class 1	Class 1	Class 3	Class 3	Class 4



The laboratories provided information about individual corrosion class determination dates. When information was sought to explain the reasons for the very wide scatter in the test results, the possibility was considered that changes in the observed degree of corrosion might take place with time. Based on the information received from the participants in the interlaboratory research, however, a statement may be made that the corrosion class determination dates (not later than 3 weeks from the sample taking date) did not affect the test results. No dependence was observed, either, between the corrosion class determined and the test time. This has also been confirmed by the examination of stability of the LPG samples, carried out after completion of the tests described herein to make sure that the characteristics of this fuel remain unchanged with time.

Additionally, investigations were carried out to determine the possible impact of the sulphur content and the presence of hydrogen sulphide and water on the copper corrosion process. With this end in view, various LPG samples were subjected to sulphur content tests to the ASTM D 6667 test method and to hydrogen sulphide and water detection tests according to PN-EN ISO 8819 and PN-EN 15469 Standards, respectively. The results of these tests have been presented in Table 9.

Table 9. Results of corrosion class and sulphur content determination tests and hydrogen sulphide and water detection tests

Sample ID	Corrosion class	Sulphur content [mg/kg]	Hydrogen oxide	Water
Sample 1	1	91	not detected	not detected
Sample 2	1	67	not detected	not detected
Sample 3	1	5.0	not detected	not detected
Sample 4	1	33	not detected	not detected
Sample 5	2	47	not detected	not detected
Sample 6	2	75	not detected	not detected
Sample 7	2	42	not detected	not detected
Sample 8	2	34	not detected	not detected
Sample 9	2	70	not detected	not detected
Sample 10	2	50	not detected	not detected
Sample 11	2	199	not detected	not detected
Sample 12	3	44	not detected	not detected
Sample 13	3	24	not detected	not detected
Sample 14	3	99	not detected	not detected
Sample 15	3	54	not detected	not detected
Sample 16	4	73	not detected	not detected
Sample 17	4	183	present	not detected
Sample 18	4	37	not detected	not detected
Sample 19	4	44	not detected	not detected

The above results show that there is no correlation between the sulphur content and the presence of hydrogen sulphide and water in LPG on the one hand and the LPG corrosiveness to copper on the other hand. For some of the samples, the sulphur content even exceeding 50 mg/kg did not contribute to the occurrence of corrosion processes on the test copper strip. On the other hand, however, in the case of some of the samples where the corrosion took place (and e.g. corrosion class 3 was recorded), the sulphur content was found not to exceed the acceptable sulphur content limit of 50 mg/kg and the presence of hydrogen sulphide or water was not detected, either. There was only one case that the presence of hydrogen sulphide was detected for an LPG sample whose corrosiveness to copper was on a level resulting in the copper corrosion class 4. Among the LPG samples selected for the tests, the highest sulphur content, amounting to 199 mg/kg, was recorded for a sample that gave copper corrosion class 2 on a four-point scale, at simultaneous absence of hydrogen sulphide and water in the said sample. This may indicate incomplete knowledge of the mechanisms that govern the course of the copper strip corrosion process. The absence of an unequivocal correlation between the parameters mentioned above and the adverse impact of the propane-butane gas on copper may suggest that LPG may contain components that are not determined during standard inspections carried out at filling stations. The PN-EN 590 does not indicate any tests that would make it possible to predict the occurrence of corrosion to copper.

## 5. Recapitulation

The interlaboratory comparisons carried out have confirmed that a problem occurs in the evaluation of the corrosion impact of LPG on copper according to Standard PN-EN ISO 6251. For the same batch of material tested at various laboratories, wide scatter was recorded between the test results obtained. It should be emphasized that even the very method of examining the copper strip condition after the corrosion test is debatable.

The visual examination can only produce a subjective assessment and it often happens that the selection of a specific ASTM D 130 Copper Strip Corrosion Standard whose look would correctly match the actually observed nature of the corrosion changes in the test copper strip is very difficult. The corrosion standards used as a reference are not always consistent with the description given in Standard PN-EN ISO 6251. The test results could also be affected by procedural errors, e.g. improper preparation of the copper strips for testing, differences in copper strip dimensions, improper filling of the test bomb, etc. Maybe an impact of considerable importance was exerted by the containers ("samplers") used to store the LPG samples and by differences in the interactions between the contaminants present in a sample and the sampler material components. Furthermore, no correlation was revealed between the occurrence of copper corrosion and the sulphur content and hydrogen sulphide and water presence in the LPG sample. It is recommendable to undertake works aimed at developing an alternative method that would make it possible to determine the corrosive properties of LPG in an unequivocal and reliable way.

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Tekst artykułu w polskiej wersji językowej dostępny jest na stronie  
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