

Secondary reactions occurring in the process of storage gas samplers to collect LPG

The sources of undesirable impurities, in the form of different chemical compounds or substances present in the LPG may be:

- Refining and petrochemical processes, ie.: ammonia, water, sulfur, methanol, fluorides, higher hydrocarbons, mechanical impurities,
- Extensive distribution systems, ie.: metal particles (Cu, Zn, Pb, Fe)
- As well as secondary pollutants, as a result of retention of large amounts of sediment inside the LPG tanks, but also within traditional gas samplers.

The presence of this kind of impurities, results in deviations from LPG quality requirements in the range of corrosive action on copper. The result of the corrosivity test are affected mainly by the sulfur, hydrogen sulfide, ammonia and amines.

Due to the growing importance of LPG and the increasing quality requirements for this kind of fuel, purpose of the work performed was to investigate the effect of the probe construction on the processes within due to the accumulation of sediment. The study used two types of samplers, traditional non-dismountable sampler and innovative dismountable sampler. For each gas sampler collected 250 samples of gas. Probes were washed before each sampling. After a series of samples the inner surface of the cylinder was observed.

The following photographs showing the inner surface of the non-dismountable and dismountable sampler after a series of sampling. For comparison purposes, a sectional view of a clean, unused non-dismountable sampler was placed. The brown sediment which adhered to the walls of the probe was removed and subjected to basic element analysis.



Traditional non-dismountable sampler



Dismountable sampler

Elemental analysis of the sediment from the non-dismountable sampler show content: Na, K, Mg, Ca, Al, V, Ni, Co, Mn, Fe, S. Pay special attention to the sulfur present in the sediments. It occurs mostly in the form of inorganic compounds, which under certain conditions could enter into secondary reactions with release of hydrogen sulfide and sulfur.



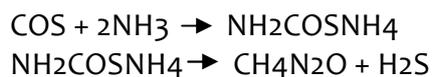
The color of the sediment taken from the non-demountable sampler: dark russet

Carbonyl sulfide present in the composition of LPG is not a factor of corrosion. However, the hydrolysis reaction of COS are formed compounds such as hydrogen sulfide and carbon dioxide



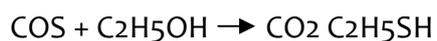
The reaction accelerates moisture, oxides and sulfides of iron, the presence of oxygen, alkalis

Carbonyl sulfide reacts with ammonia to form a thio ammonium carbamate compound which upon heating decomposes into urea and hydrogen sulfide.



The addition of alcohol reduces the rate of hydrolysis of the COS in the water and in the environment, for example, pure methanol, this reaction occurs very slowly.

Carbonyl sulfide reacts also with aliphatic alcohols to form mercaptans.



under alkaline conditions this reaction proceeds very rapidly and to completion

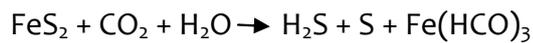
Mercaptans did not cause corrosion, however, they react with the elemental sulfur form corrosive hydrogen sulfide.

Present in LPG the hydrogen sulfide, even with trace amounts of oxygen are oxidized to sulfur. In the storage and transport tanks for LPG oxidizing agent can provide iron oxides present on the inner surface of the tank.

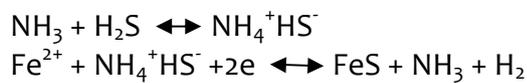


The catalyst for these reactions is moisture and soot

In view of corrosive changes in LPG, it is also dangerous presence of carbon dioxide.



Corrosive effect has also ammonia, that at high concentrations with hydrogen sulfide forms ammonium sulfide corrosion.



Summarizing the above analysis it should be emphasized that the sediments accumulated on the inner surface of the non-demountable samplers and occurring as a result of secondary reactions, may falsify the results of measurements of the LPG where a particular importance for the objective assessment of the quality to results of the determination of total sulfur content and corrosive action on copper. These parameters are also the most common causes of exceeding the quality standards LPG fuel. Therefore, the possibility to dismantle and thoroughly cleaned the sampler before each sampling, allows for highly representative samples, and thus a more reliable test results.