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COMPARATIVE ANALYSIS OF DEVICES USED FOR HYDROCARBON CONCENTRATION MEASUREMENTS DURING CARGO TANK GASSING-UP OPERATIONS ON GAS CARRIERS

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Abstract: The paper is a detailed analysis of the devices used in measurements of hydrocarbon content on gas carriers during cargo tank gassing-up operations. The characteristics of the Riken Keiki GX-8000 portable gas detector used commonly on ships are described, the types of detection used in the device in relation to the detected gases are discussed, which made it possible to question the validity of using the detector for analysing the concentrations of large quantities of hydrocarbons on gas carriers. Also discussed is a device enabling such analyses to be carried out much more accurately – the Agilent 490 Micro GC chromatograph, which will substantially improve the process of cargo tank gassing-up.

Keywords: portable gas detector, chromatograph, gassing-up, Ethylene, Nitrogen.

1. INTRODUCTION

One of the more complex processes conducted on gas carriers is gassing-up cargo tanks with cargo vapours, the density of which is substantially similar to the inert gas density, which the tanks are filled with to create an inert non-explosive atmosphere (cargo tank inerting). The issue applies primarily to ethylene as cargo, and nitrogen as the inert gas [Wieczorek 2017; 2018]. The procedures for inerting and gassing-up of cargo tanks, as well as nitrogen and ethylene densities at specific temperatures are discussed in detail in the following papers: A. Wieczorek, *The problem of insufficiently optimal gassing-up operation carrying after tanks inerting with reference to ethylene carriers*, Scientific Journal of Gdynia Maritime University, no. 100/2017, pp. 179–186 and A. Wieczorek, *Alternative solutions of optimisation of the gassing-up operation after tanks inerting of pressure swing adsorption (PSA) and membrane techniques*, no. 105/2018, pp. 136–144.

Cargo tank gassing-up operations should be conducted in a manner that enables subsequent cooling of the tanks and cargo without additional cargo losses.

In the case of ethylene and nitrogen, nitrogen content in the mixture of the two gases must not exceed 2% [Wieczorek and Giernalczyk 2018]. Hydrocarbon concentrations in the gassed-up tanks are read using the Riken Keiki GX-8000 portable gas detector. This instrument, as well as an alternative device designed for measuring the content of hydrocarbon and various other chemical compounds, are described in detail in the following sections.

2. RIKEN KEIKI GX-8000 PORTABLE GAS DETECTOR

The Riken Keiki GX-8000 portable gas detector (Fig. 1) is a gasometric instrument with integrated electrochemical sensors or a galvanic cell containing electrolytes. It enables analysing the concentrations of such gases as: oxygen, flammable gases, toxic gases (carbon monoxide and hydrogen sulfide) in the air, as well as high concentrations of flammable gases in nitrogen and inert gases.

Table 1 shows the classification of the detected gases according to the detection type used in the device. The detector comprises a measurement instrument, a sampling probe and a hose connecting the two elements, which a mixture of chemical compounds flows through (Fig. 2). The error margin in this device is 5% [Portable Gas Monitor GX-8000 Operating Manual].

The GX-8000 portable gas detector is commonly used on ships for measuring hydrocarbon concentrations during cargo tank gassing-up operations.

Fig. 1. Portable gas detector Riken Keiki GX-8000 [Portable Gas Monitor GX-8000 Operating Manual]

Table 1. Gases detected by the GX-8000 detector according to the type of the detection used in the device [Portable Gas Monitor GX-8000 Operating Manual]

Detection type	Galvanic cell	Ceramic catalyst	Electrochemical sensor	Electrochemical sensor
Gas detected	Oxygen (O_2)	Flammable gases ($HC/CH/H_2$)	Hydrogen sulfide (H_2S)	Carbon oxide (CO)

The device is designed to measure gas concentrations at atmospheric pressure. To obtain a correct result it must be calibrated, the device's operating parameters must be adjusted for the operating conditions. The device does not have to be calibrated on the chemical compound whose concentration is to be measured. The calibration can be performed on another hydrocarbon. If calibration is performed using, for example, isobutane, the measurement results must be read using the following curve – 100% isobutane concentration corresponds to 75% ethylene concentration in the test sample (Fig. 3) [Portable Gas Monitor GX-8000 Operating Manual].

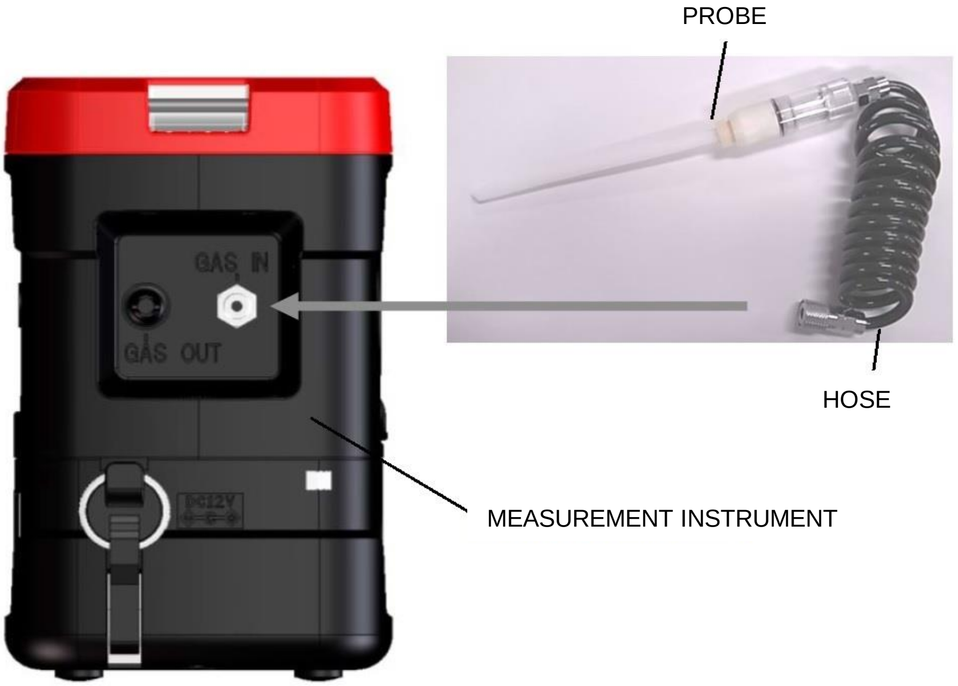

Fig. 2. Elements of the Riken Keiki GX-8000 gas detector [Portable Gas Monitor GX-8000 Operating Manual]

A common issue on ships when measuring hydrocarbon concentrations during cargo tank gassing-up is the device's excessing inaccuracy [Shipowner's documentation]. To properly conduct this process, measurements of inert gas concentration in such mixtures with cargo as nitrogen and ethylene, must have an accuracy of at least 2% [Wieczorek and Giernalczyk 2018]. The GX-8000 gas detector does not provide this ability. Furthermore, this model in the GX-8000 version is not suitable for analysing high hydrocarbon concentrations [Shipowner's documentation; Portable Gas Monitor GX-8000 Operating Manual].

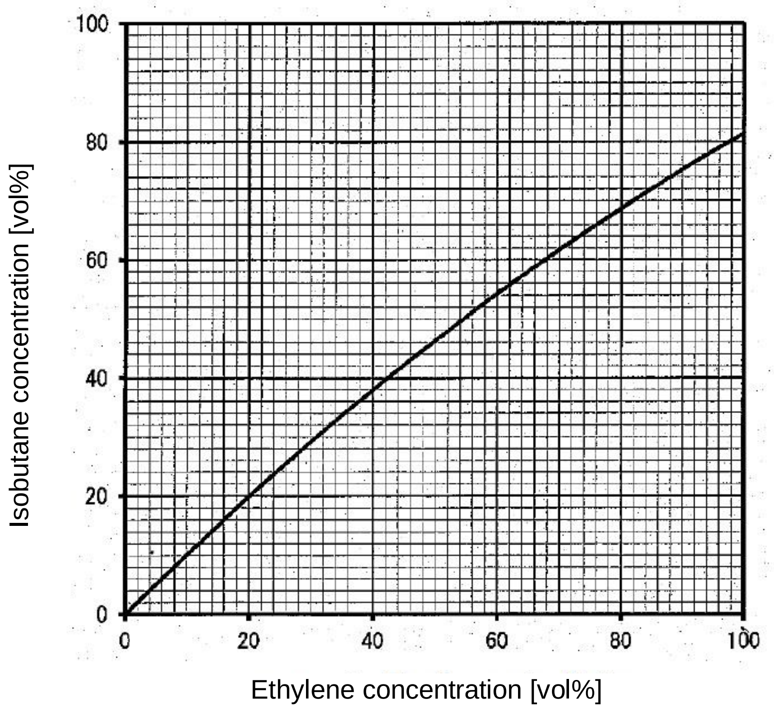

Fig. 3. Calibration of the Riken Keiki GX-8000 gas detector [Shipowner's documentation]

When verifying high hydrocarbon concentrations, there is a risk of damaging the carbon oxide or hydrogen sulfide measurement sensor [Portable Gas Monitor GX-8000 Operating Manual]. Consequently, it is necessary to use instruments enabling much more accurate measurements, with a design and properties suitable for measuring high hydrocarbon concentrations.

3. AGILENT 490 MICRO GC CHROMATOGRAPH

The 490 Micro GC chromatograph is a device used to separate or test the compositions of mixtures of various chemical compounds. It is designed for analysing gases and vapours. The device enables effective performance of analyses by separating the test sample of chemical compounds. Samples are transported using a carrier gas. The following gases can be used in this role: hydrogen, helium, methane, oxygen, nitrogen, carbon oxide, ethane, propane, argon, carbon dioxide, butane. Depending on the type of analysis to be performed, a suitable carrier gas must be used [Agilent Technologies]. In practice, the most commonly used are helium, hydrogen – which halves the retention time compared to helium and the other carrier gases – as well as nitrogen and (in columns with molecular sieves) argon, which prolong the retention time, compared to helium and hydrogen. The difference between the relative thermal conductivity of the carrier gas and components of the sample should be as high as possible [Consultations at the Institute for Chemical Processing of Coal 2018].

Table 2 shows several examples of thermal conductivity of gases.

Table 2. Relative thermal conductivity of carrier gases [Agilent Technologies]

Carrier gas	Relative thermal conductivity
Hydrogen	47.1
Helium	37.6
Methane	8.9
Oxygen	6.8
Nitrogen	6.6
Carbon oxide	6.4
Ethane	5.8
Propane	4.8
Argon	4.6
Carbon dioxide	4.4
Butane	4.3

The carrier gas must contain no impurities, in particular oxygen, water vapour or hydrocarbons. It is for this reason that carrier gases such as ethane, propane or butane are not used for the analyses, as they usually contain admixtures of other hydrocarbons, which greatly extends the retention time and causes 'noise' on the resulting charts, The highest thermal conductivity is shown by hydrogen and helium, the lowest – by butane, carbon dioxide, argon and propane. Hydrogen, as a flammable gas, requires particular attention and leak control inside and outside the 490 Micro GC device using an electronic leak tester. The chromatograph can be equipped in four independent column channels – analytical modules. Each channel is miniaturised, with an electronic gas control panel, a microperforated injector, narrow analytical column and thermal conductivity microsensor [Agilent Technologies; Consultations at the Institute for Chemical Processing of Coal 2018].

Unlike the Riken Keiki GX 8000 portable gas detector, the Agilent 490 Micro GC chromatograph enables readouts with a very high accuracy, approximately 0.01% [Agilent Technologies].

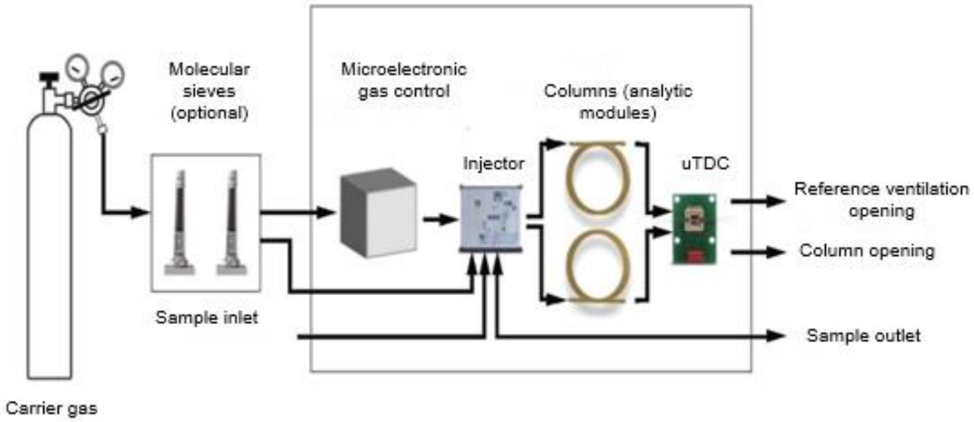

Fig. 4. Chemical compound analysis process in the chromatograph [Agilent Technologies]

For testing chemical compound samples on gas carriers, the chromatograph uses the Pora Plot U column. 99.999% pure helium is used as carrier gas. The chromatograph's principle of operation is based on the phenomenon of molecular interactions between the chemical compounds that form the analysed mixture and the column packing. Introducing the test sample into the carrier gas stream is made possible by the injector, which moves the sample into the column. The time it takes to enter the sample in the injector should be as short as possible, and the sample's volume as small as possible. It is paramount that the volume of gas in subsequent injections be identical. Gas samples are dosed into the injection system using a suitable syringe. The sample is then 'taken' by the carrier gas towards the column, where separation of the mixture to be chromatographically analysed occurs. Such columns are made of glass and take the form of 10 m long capillary tubes. Immediately downstream of the column is a detector responsible for identifying the individual substances separated in the chromatographic column and measuring the concentrations of the mixture components in the carrier gas. The detectors react to differences in physicochemical properties of uncontaminated carrier gas and gas that contains a substance eluted from the column. The time it takes the test chemical compound to pass through the column is called retention time [Agilent Technologies; Consultations at the Institute for Chemical Processing of Coal 2018].

The process of sample analysis in the chromatograph is shown in Fig. 4. The chromatograph with a sample attached (a mixture of nitrogen and ethylene) is shown in Fig. 5. An open Agilent 490 Micro GC chromatograph is shown in Fig. 6.

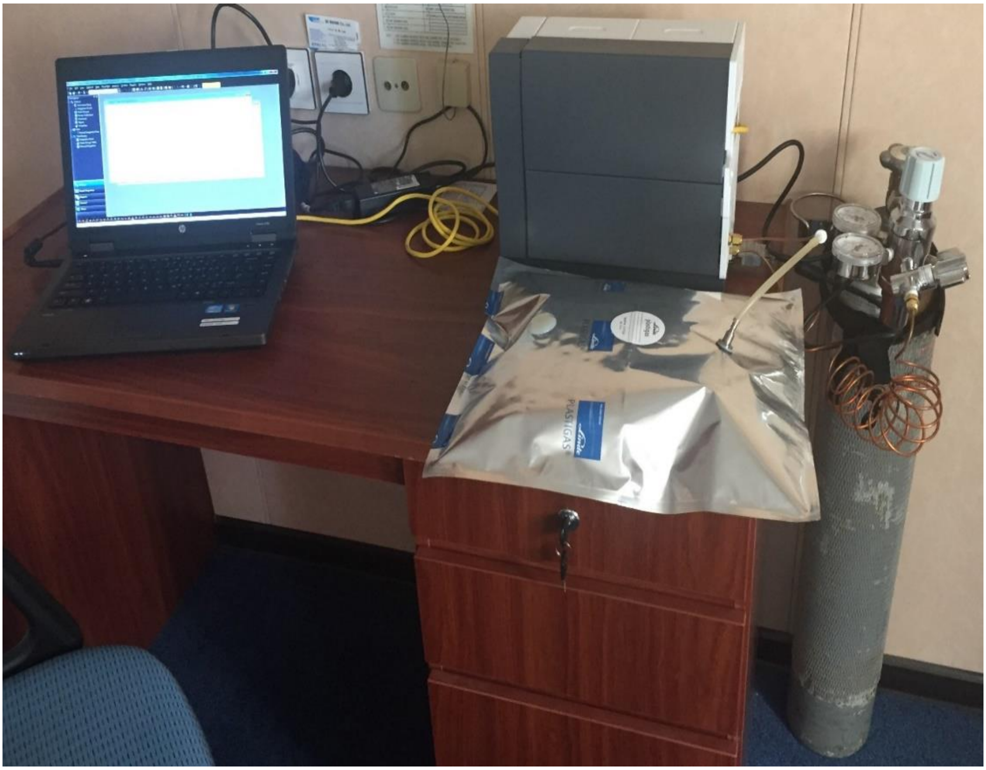

Fig. 5. Agilent 490 Micro GC chromatograph with a bag containing a cargo sample

Substances separated in the chromatographic column are qualitatively identified by the position of the peaks corresponding to a given substance on the chromatogram, i.e. using the known retention times in the given medium [Agilent Technologies]. An example of peaks for a mixture of 98% ethylene and 2% nitrogen with specific surface areas, which enable determining the concentration of the individual components using the previously performed calibration, is shown in Fig. 7. A drawback of the device is its size, the necessity of using additional carrier gas cylinders, and test (calibration) cylinders containing mixtures of the analysed gases, which enable controlling the correctness of the analyses performed.

Furthermore, small amounts of air penetrate into the system together with the analysed samples, which affects the results of initial measurements [Shipowner’s documentation; Consultations at the Institute for Chemical Processing of Coal 2018].

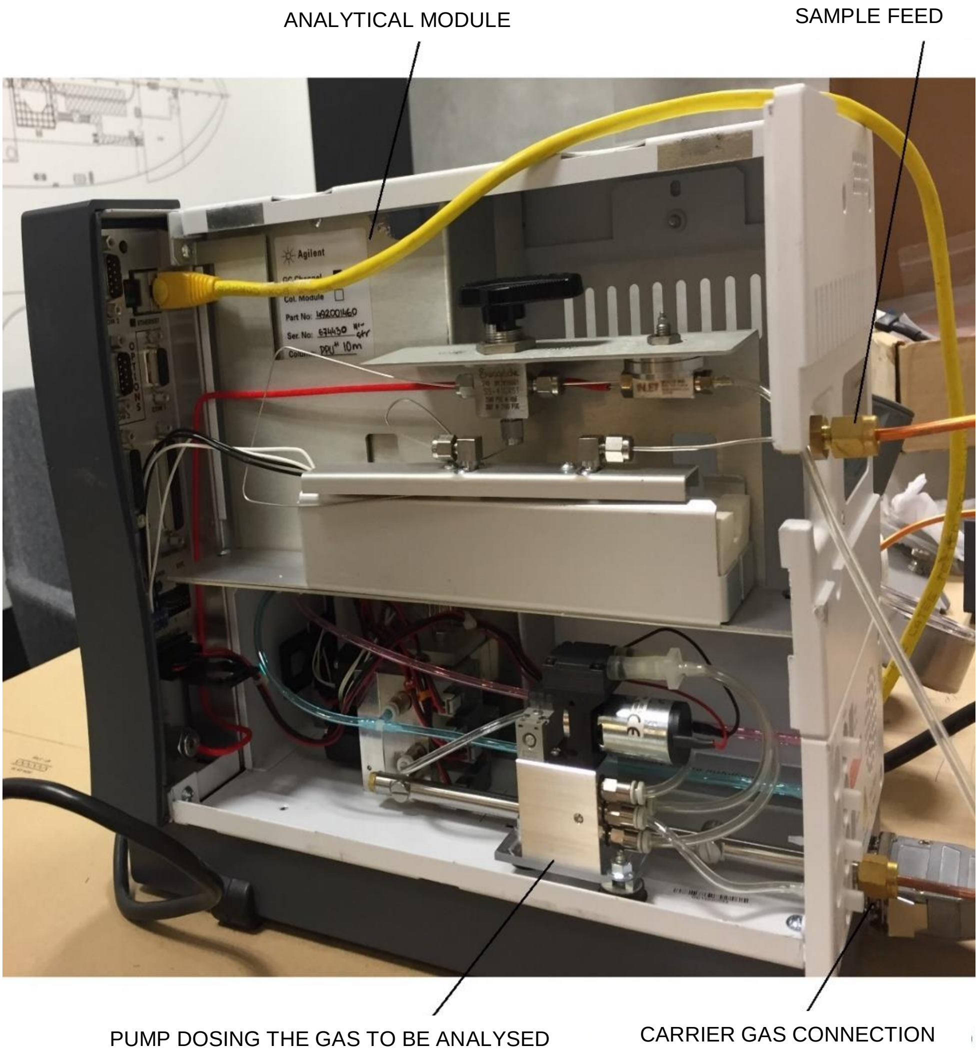

Fig. 6. Opened chromatograph Agilent 490 Micro GC

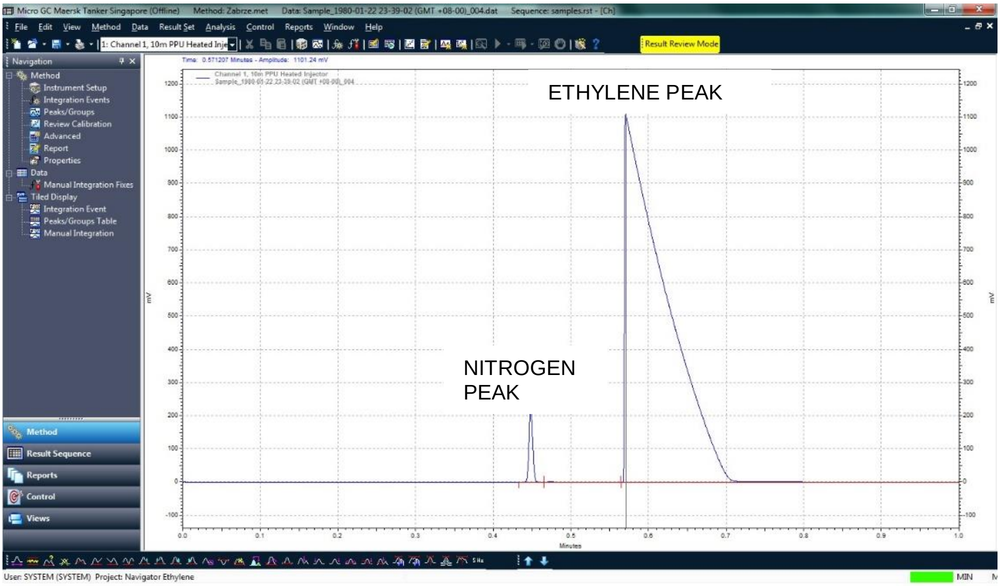

Fig. 7. A chromatogram received during analysing a test sample – 2% of Nitrogen and 98% of Ethylene

4. SUMMARY

For the purpose of performing analyses on gas carriers, the Riken Keiki GX-8000 gas detector is an insufficient device due to its inadequate hydrocarbon concentration measurement accuracy. A much more accurate instrument for measuring hydrocarbon content in mixtures with carrier gases during cargo tank gassing-up operations is the Agilent 490 Micro GC chromatograph. Hydrocarbon content determination with an accuracy of 0.01% greatly streamlines the process, improves equipment operation and reduces the amount of cargo lost to the atmosphere during gas carrier cargo tank gassing-up.

Heretofore hydrocarbon concentration analyses in cargo tanks were performed on a chromatograph equipped with a Pora Plot U column. To eliminate the impact of air on results during initial measurements, the device should be equipped with a new module – the 5A column, whose internal walls are covered with a zeolite molecular sieve, which prevents penetration by air components, except nitrogen, which is also a component of the test sample, and consequently the presence of nitrogen from the air does not affect retention time.

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Wieczorek, A., 2018, *Alternative Solutions of Optimisation of the Gassing-up Operation after Tanks Inerting of Pressure Swing Adsorption (PSA) and Membrane Techniques*, no. 105, pp. 136–144.

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