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Determination of MDEA and piperazine content in aqueous amines

Parameter monitoring procedure in natural gas amine treatment to remove CO_2 during Liquid Natural Gas (LNG) production differs from analytical algorithms developed for removal processes of sour components (CO_2, H_2S, SO_2, R-SH) from associated gases or from refinery hydrocarbon gases. Both technical approaches include compositional analysis of amines and gas streams at inlet and outlet of an amine treating unit. If mains gas with low concentrations of hydrogen sulphide and other sulphur-containing substances is used as a feedstock, then in the LNG Compressor it is only sufficient to monitor CO_2 content in treated gas. Notwithstanding, in order to monitor parameters of aqueous amine absorption and regeneration processes in the LNG Compressor it is necessary to perform quantitative assays of basic components of unreduced amines – MDEA, piperazine – and identify their salts (carbamates and bicarbonates).

Many refineries and gas treatment plants use the routine laboratory procedure based on titration quantitative method. Parameter monitoring procedure represents a modification of standards ASTM [1–3]. CO_2, H_2S and total aqueous amines are determined on the basis of endpoint by acid-alkali titration with the use of indicators (colourimetry) or on the basis of the equivalent point with the use of pH-meter or ion-specific electrode (potentiometry). The procedure is labor intensive and has significant restrictions on selectivity of target component determination and measuring accuracy due to interferences of unknown substances present in the sample tested. In practice, this titration procedure implements the discriminant monitoring method; and if threshold levels established have been exceeded, gas chromatography should be used as the test arbitration (reference) method; this method may be also used for determination of amine degradation products [4].

The paper [5] suggests principles to improve the test titration method; these principles are based on independent measurements taken for separate identification of reduced, hydrogenized amines, total amines, CO_2, H_2S, total ions of heat stable salts. A complete set of equipment for the improved procedure includes: a conductometer, a pH-meter, a set of selective and reference electrodes, Karl Fischer titrator in addition to an autotitrator.

Techniques to automate the monitoring of amine treatment are available. Galvanic Applied Sciences (Canada) suggests an on-line automated titrator (industrial version) for determination of total amines, CO_2, H_2S [6]. In spite of automation and responsiveness of measurements, the analyzer still has had all shortcomings inherent to the laboratory method. There is another approach based on the use of an on-line gas chromatograph with liquid sample evaporation in flow under 'liquid-gas' equilibrium and quantitative assay of aqueous amine components. For direct injection of aqueous amine samples into the chromatograph either a separate unit or a dosing injector may be used to prepare liquid samples [7].

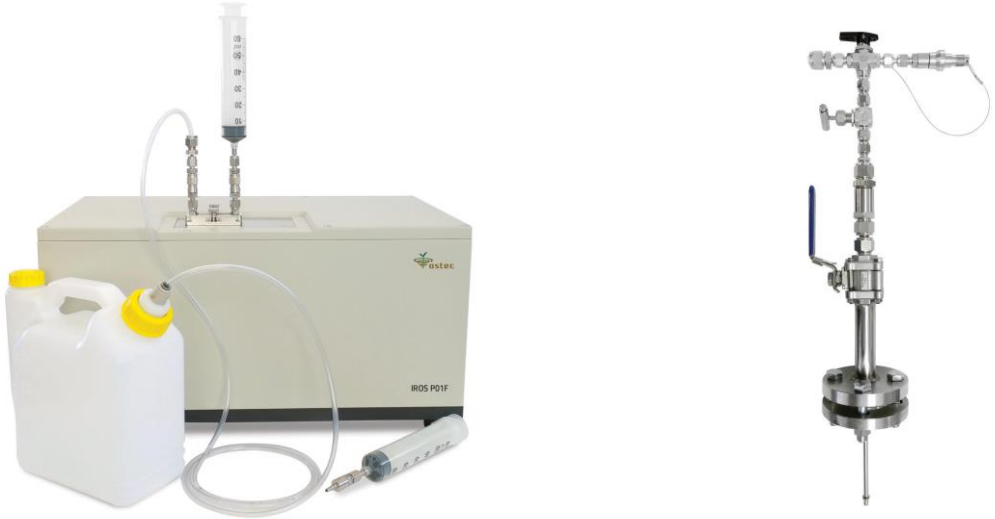
Ion [8] and high-efficiency liquid chromatography (HELC) [9] is another laboratory method of aqueous amine determination. Main restrictions on application of these methods in industry are high requirements for qualification of operators and the necessity for applying consumables-chemical agents for separation in liquid phase as well as high purity deionized water.

Optical molecular spectroscopy is an alternative method that may solve the problem pertaining to monitoring of operational parameters of amine treatment. The review [10] considers the opportunities and comparative specifications of various spectral methods: Raman spectroscopy, near infrared (NIR) spectroscopy, Fourier-transform infrared (FTIR) spectroscopy in combination with attenuation total reflection (ATR) method. There is a general possibility of applying all above mentioned methods to complete this task; however, full-scale tests conducted at the pilot (experimental industrial) facility have demonstrated a real advantage of FTIR spectroscopy in combination with ATR method in comparison with NIR spectroscopy and Raman spectroscopy. Restrictions of the last method are due to interferences resulted from fluorescence in the course of laser irradiating of the sample; such laser irradiating is powerful enough to reach measuring sensitivity required [11].

The ATR method makes it possible to perform rapidly assays without sample preparation even with strong absorption of IR radiation by water. For determination of MDEA and piperazine an aqueous amine sample is dosed out directly onto prism surface of the ATR unit. Capabilities of FTIR spectroscopy in combination with ATR method (in-situ version) were tested at the pilot full-scale plant, Equinor (until 2018 – StatOil, Norway) [12] and pilot amine treating plant (flue gases), EnBW, Heilbronn (Germany) [13].

Researches in progress intended for selection of analytical monitoring method and control of amine treatment process reflect the fact that the laboratory titration method still remains the standardized method though a large amount of scientific works have been completed in this sphere; this laboratory titration method is not suitable for automated LNG production.

In the strategy to exercise analytical control over processes, field analyzers for measuring discrete samples (at-line /on-site version) with the device located in the vicinity of the plant, are allowable for use. Main advantages of such approach are low capital costs and cost of ownership with timely provision of relevant information about the process parameters and conditions. Papers [14, 15] present the possibility of using advanced FTIR spectrometers with the ATR unit for field monitoring (control) of amine treatment.



(a) *(b)*

Analyzer of MDEA and piperazine content in aqueous amine:
a – the device complete with auxiliary equipment;
b – the process medium sampling probe with ball shutoff valves and control needle valve.

Figure above shows the analyzer of MDEA and piperazine content in amine aqueous solution on the basis FTIR spectrometer and auxiliary equipment for sampling and injection of samples into the flow part of the ATR unit. Such amine analyzer with built-in gaging has been specially developed on the basis of multi-purpose lab FTIR spectrometer IROS P01. The device upgrading includes addition of built-in ATR unit with the flow cell and specialized software and "button-type" control. After starting the measuring process by pressing "Start" button, the operator performs operations in sequence in accordance with the algorithm; the latter is completed by automatic computation of MDEA content and piperazine in the sample tested and the measurement; further the report is displayed on the screen or printed out.

The integrated interface (quick connectors with double-sided fastening) is used both for the sampling probe and flow cell of the analyzer. One shutoff valve is located on the nozzle of probe or flow cell and the other – on a sampler-transport container; a syringe (a syringe filter for chemical analysis) made of inert plastic serves as such sampler-transport container.

The developed analysis system, including the original sampling probe (which may be installed on the amine treatment system drain connection with the shutoff ball valve) ensures representative sampling of small volume (about 50 cm^3) and tightness of all connections including connections intended for injection of the tested aqueous sample into the flow cell.

Measurement cycle duration of a single sample including sampling and transportation operations is 5-10 minutes with the consideration of measurements taken in parallel for on-line control over the accuracy. Measurement result inaccuracies obtained with the use of the analyzer and confirmed by the validation procedure are within the range of accuracy indicators of the lab gas chromatographic analysis.

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