DRY COLORIMETRY DETECTION FOR ARSINE QUANTITATION IN GASES

Arsine (AsH_3) is one of the most dangerous gases commonly found during hydrocarbon extraction and treatment operations. This requires strict control given the low exposure limits (below 0.05 ppm) established for the Occupational Safety and Health Administration[1]. The presence of arsine in refineries and gasification processes represents a critical control point in economic terms, and additionally it may contribute as a potential environmental issue. Dry colorimetry offers an analytical solution, at low cost, for arsine quantification at trace levels for laboratory and on line applications with reliable results.

Arsine is a highly flammable colourless gas that has a garlic odour. The gas is also known as arsenic hydride, arsenic trihydride, hydrogen arsenide and arsenous hydride[2]. Within the major anthropogenic sources of arsine, the metallurgical industry and the battery production as an alloy with lead, count as the main activities that may be directly involved with arsine emissions.

Arsenic species is ubiquitous to industrial gases, hydrocarbon feed stocks, fuels and natural gas. Its concentration is strictly controlled, more specifically for cracking and fractioning operations (figure N.2), because most of the petroleum fractions treatments involve a noble metal catalyst that loses their efficiency for reaction with arsine as the main gaseous form[3].

The principle of dry colorimetric method relies on different color intensities which are proportional to the impurity concentration in the sample. The colorimetric detection is carried out with an optic photodiode system (figure N.3) sensing the colour changes of a chemically impregnated paper that reacts selectively to the target impurity present.

Figure N.1 Arsine molecule

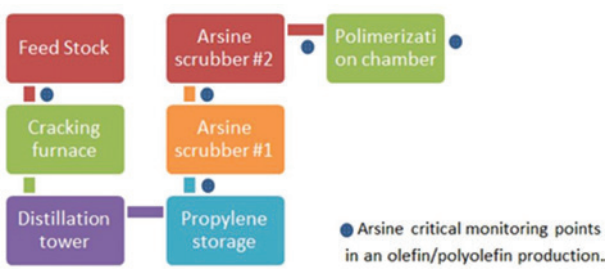

Figure N.2 Olefin/polyolefin critical Arsine points

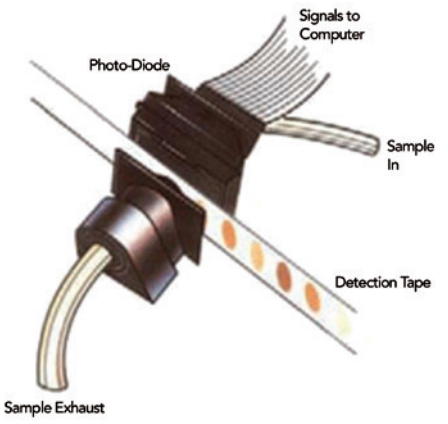

Figure N. 3 Schematic of optics photodiode system for dry colorimetric detection.

Results

The majority of hydride applications for dry colorimetric detection are performed using permeation devices as standard gases. In accordance with experimental results arsine is measured in different gases as background, such is the case of propylene (Liquefied Petroleum Gas, LPG) and nitrogen. Since no differences are observed regarding the arsine concentration, the matrix effect is negligible (figure N.4).

Because arsine is a very toxic gas, and the necessity of monitoring this type of substances at hazardous locations avoids its access at controlled environments even for calibration purposes, we proposed the use of a surrogate compound, hydrogen sulfide H_2S, to indirectly measure the arsine concentration. This methodology has been tested and experimentally presents good linearity at low arsine levels (figure N. 5). In addition, the technique presents a repeatability of ±3 % in a full scale of 100 ppbv (figure N. 6).

When using a surrogate (H_2S), arsine detection follows a linear trend and with this methodology, it is possible to measure concentrations as low as 1 ppbv AsH_3.

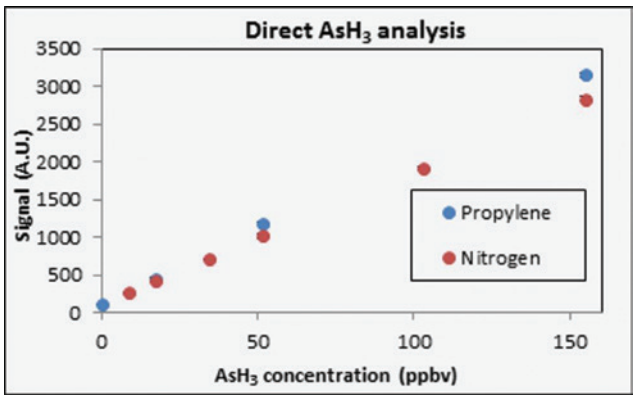

Figure N. 4 Direct arsine detection in different gases as background.

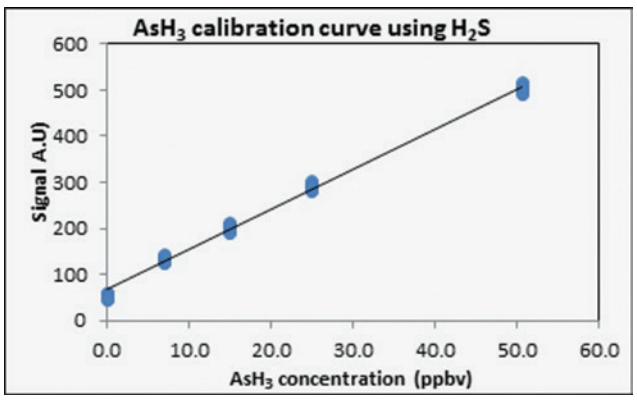

Figure N. 5 Arsine calibration curve using H_2S as surrogate.

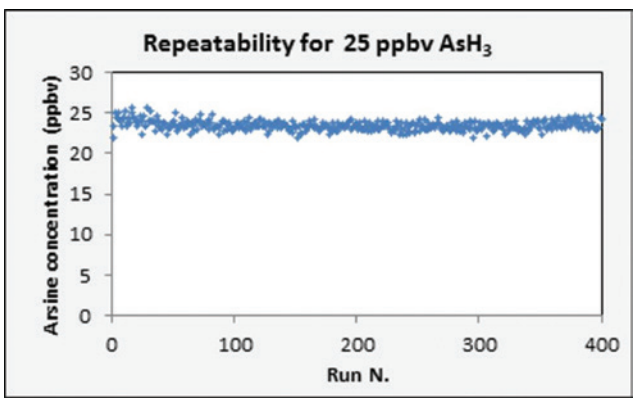

Figure N.6 Repeatability results at 25 ppb AsH_3, measured with H_2S in nitrogen.

Conclusion and Perspective

- Arsine detection using the dry colorimetric method has high sensitivity, a broad linear range (including low ppb concentrations), fast response, high accuracy and a good degree of repeatability and reproducibility. Both laboratory and on line testing units present similar results.
- If mono or di-substituted standard compounds are commercially available, perform testing on alkyl substituted arsine gases (p.e. monoethyl arsine, tert-butylarsine, diethyl arsine). These chemical species are reactive with the tape detection used for arsine.

References

[1] osha.gov/dts/chemicalsampling/data/CH_219590 consulted on 2017-11-23 at 16:31.

[2]pubchem.ncbi.nlm.nih.gov/compound/Arsenic_trihydride. Consulted on 2018-02-20 at 14:57.

[3] Johnson et al. Patent number 4,593,148, Process for removal of arsine impurities from gases containing arsine and hydrogen sulfide.

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