

Measurement of BTEX in Amine and Dehydration Solutions of Natural Gas Processing Plant

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Abstract:

Benzene, toluene, ethylbenzene, and o, m, and p-xylenes (BTEX) not only are hazard to the environment and the public health but also could produce foaming technical problem in natural gas processing². BTEX in the natural gas is absorbed by amine sweetening and glycol dehydration units. Several operating parameters directly affect the amount of the BTEX absorbed in a unit. These factors include the inlet BTEX composition, contactor operating pressure, circulation rate, solvent type and temperature. Measurements of the BTEX in the processing solutions are important in emissions and operational condition of units. We have developed a very simple extraction and analysis method for BTEX which can be extended to VOCs. An organic solvent such as n-Hexane or n-octane depends on the absence of this compound as VOC in the solutions were selected as extractor. A gas chromatograph with an FID detector and appropriate column for separation of the BTEX and an internal standard calibration method was used for analysis of extracted solutions. Without doing any preconcentration, this method covers the determination of the BTEX in the processing solutions ranging from saturated condition to the detection limit of the GC (1ppm) for each one of the compounds. Standard deviations of the analysis were less than 3% depending on sampling condition.

Keywords: BTEX, amine and glycol solutions, liquid/liquid extraction, GC

Introduction

Most natural gas when initially produced from a well is not "clean", but is instead laden with associated compounds that may require removal prior to utilization of the natural gas as a fuel gas. Naturally occurring compounds in the natural gas include VOC (volatile organic compounds) and acid gas, all of which may be required to be removed in a gas treatment process. Organic compounds entrained in the gas and that are heavier than ethane are typically considered by regulatory agencies to be VOC. There is also a subset of the VOC's which are referred to as BTEX and includes benzene, toluene, ethylbenzene and xylene. In terms of environmental impact and regulatory restraints, VOC's will normally have certain limits placed upon their free release as will BTEX's, but the limits will be more stringent with respect to the subset, BTEX, of the VOC's. An example would be the allowance of twenty-five tons per year of total VOC, but only ten tons per year of BTEX in a vent stream.

Normally in gas processing plants, an amine based solvent and glycols are used as stripping agents for acid gas and water respectively. Because of the type of solvent used for the stripping, VOC is also stripped there from and entrained in the solvents. In this system and others of conventional design, the VOC and acid gas components have an affinity for the solutions and are absorbed by physical and/or chemical reaction there into.

In a conventional system, after an adequate contacting process has been undergone to expose the gas to the solvents, the highly pressurized rich absorbent fluid stream of solutions are processed to a flash tank where the pressure is reduced from approximately 900 psia to approximately 65 psia. When this occurs, the more volatile absorbed components back out of the solutions and are liberated there from. These released gases can be used as fuel gas, process gas in SRU, petrochemical or flared off. This portion of the regeneration processes for the streams remove a portion of the VOC.

However, amounts of VOC present that are too high for venting and therefore regulations require the effluent stream from the stripper to be burned in a flare to rid it of the environmentally offending VOC content. The problem encountered at this juncture of the process is that this gas stream is not sufficiently flammable to burn under its own combustibility because of the high CO₂ or water content. Therefore, fuel gas must be introduced for the effluent stream in sufficient quantities to permit its being burned in a flare. In practice, the amount of fuel gas required is significant and can add an appreciable cost to the processing of the gas. It is not unusual for this cost to amount to as much as \$100,000 per year. Therefore, it stands to reason that the owners of such gas processing plants are very interested in improving their compliance with respect to VOC and BTEX emissions. Also the concentration of BTEX in solutions can directly affect on the physical and chemical properties of solutions such as density, viscosity, flash points, dispersibility, emulsion stability, solubility, and weathering processes. Also deleterious effects of heavy hydrocarbons and particularly aromatics in a sulfur plant feed are well documented.^{1,2,3}

Catalyst coking has been tied to aromatics with toluene shown to be the primary contributor to coking. Benzene was shown by mass balance to pass through the catalyst beds unchanged and could therefore remain in the vent gas stream for a split flow plant.²

BTEX compounds frequently enter air, soil, sediments, and groundwater because of sources spill, leakage and improper waste disposal practices. BTEXs are hazardous carcinogenic and neurotoxic compounds and are classified as priority pollutants regulated by Environment Canada' and the US. Environment Protection Agency (EPA), especially benzene, which has a very low tolerance standard in drinking water of 5 µg/L. Analytical techniques for volatile organic compounds (VOCs) including BTEX have made major advances in recent years. The US.EPA has developed a series of matrix-specific methods for VOC analysis based on the original work of Bellar and Lichtenberg in the early 1970s.³ Although there are minor differences among the methods, all employ a dynamic headspace or purge and trap technique to extract the analyte from the matrix and introduce it into a gas chromatograph (GC). The American Society for Testing and Materials (ASTM) developed a series of test methods specially for determination of BTEX in gasolines, such as method D44201 for determination of BTEX content in finished gasoline by GC, method D360611 for determination of benzene and toluene in finished motor and aviation gasoline by GC, and methods D3797 and D379812 for determination of benzene, toluene, and ethylbenzene impurities in xylene by GC.

In this paper, we report our attempt to develop a rapid, reliable, and effective method for identification and determination of BTEX components in amine and glycol solutions using simple extraction and capillary gas chromatography (GC) technique. The efficiency and

reproducibility of the method were demonstrated by separation and determination of a standard BTEX mixture.

Experimental Section

Materials and Solution. Benzene, Toluene, Ethylbenzene and Xylens standards (the purities of most standards are greater than 99%) internal standard 2-propanole were purchased from Merck and directly used without further purification. Lean and rich commercial amine and glycol were prepared from South Parse plants of Iran. The BTEX solutions were prepared by dissolving benzene, toluene, ethylbenzene and p-xylene in diethanol amine or glycol, respectively. n-Hexane was used as extracting agent.

Experimental and Procedures. A calibration mixture was prepared by 2 gr. Benzene, 1.5 gr. Toluene, 0.9 gr. Ethyl benzene and 0.5 gr o-Xylene (40.82%, 30.61%, 18.37% and 10.2% BTEX respectively) based on relative concentration of BTEX in the amine or glycol of refinery solutions (table 1). 500 gr of fresh amine or glycol solution was contaminated with appropriate amount of the calibration BTEX mixture (for instance 245 mgr for 490 ppm BTEX). Three times 15 ml portion of n-hexane as extractor was shaken with 100 gr of the contaminated solution held in 100-mL separatory funnel (fitted with ground glass stoppers) and collected in a 50 ml volumetric flask (pre weighted). The 50 ml flask was filled up with n-hexane and weighted. Finally 20 μ lit 2-propanol as internal standard was added to the flask. Same procedure was done for any test or real samples. After extraction, analyte losses from the flasks were negligible.

Table 1. Range of BTEX concentration in an amine or glycol unit.

| Component | Benzene | Benzene | Ethylbenzene | Xylenes |
|------------|---------|---------|--------------|---------|
| Con. (ppm) | 200-250 | 170-220 | 80-120 | 80-120 |

Capillary Gas Chromabgraphy (GC). The separated organic phase in hexane was measured by gas chromatography on a Varian 3800 equipped with a TCD and FID detectors. A CP-Sil PONA column with dimensions of 100 m x 0.25 mm i.d. (0.25 μ m film) was used. The chromatographic conditions were as follows: carrier gas, helium (2.0 ml/min); injection mode, split 1/100; injector and detector temperature, 280 and 300 °C, respectively. The following temperature program was used for analysis of BTEX: 35 °C for 8 min, ramp at 5 °C/min to 200 °C, and hold for 10 min.

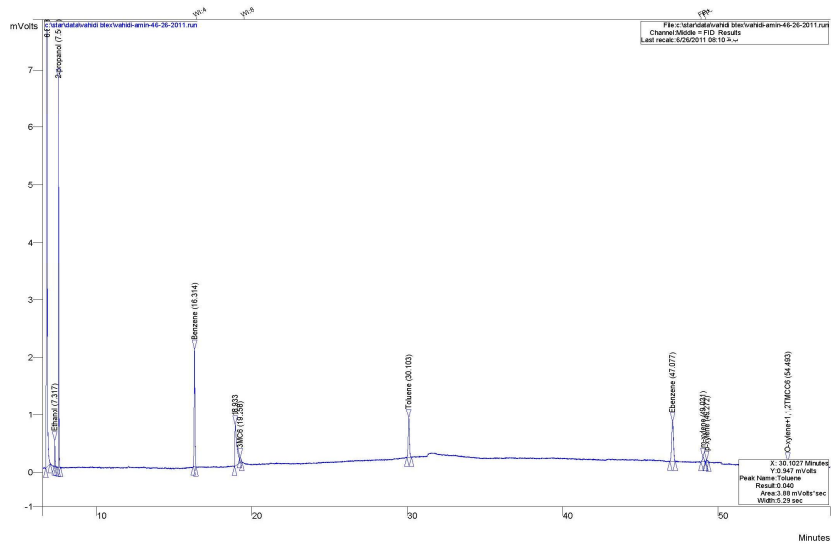


Fig. 1. A sample chromatogram of a BTEX extracted by n-hexane

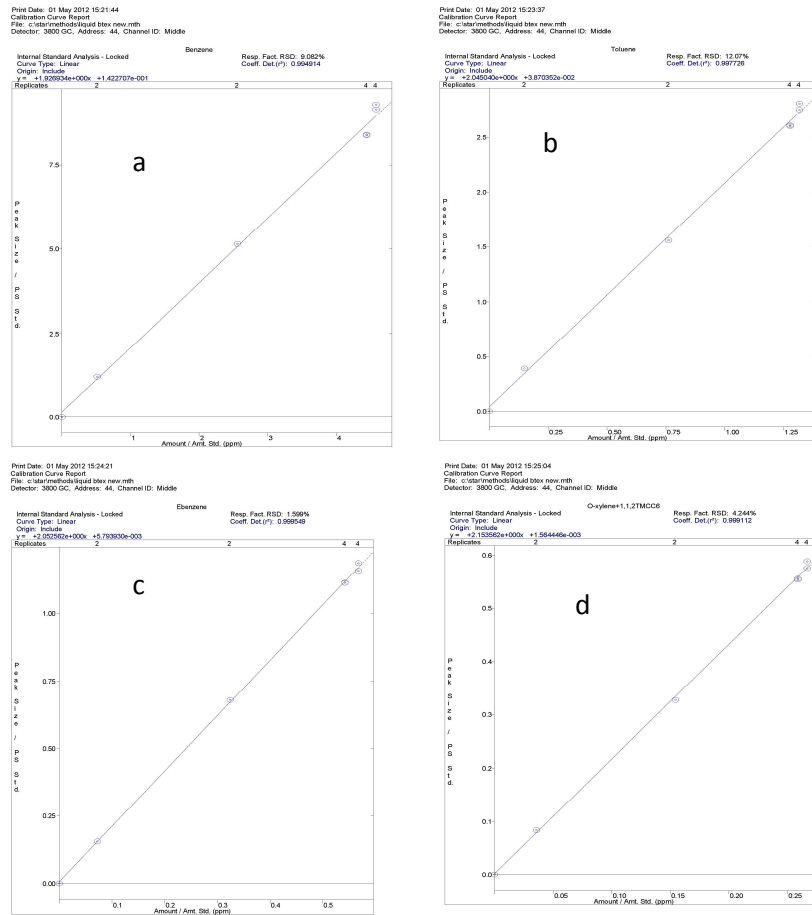


Fig. 2. Calibration curves of benzene (a) Toluene (b) Ethyl benzene (c) and o-Xylene (d).

Results and Discussion

Prior to sample analysis, the instrument was calibrated using a standard solution that was composed of five BTEX compounds. 2-Propanol was used as the internal standard. A five point calibration curve that demonstrated the linear range of the analysis was established for each target compound. All these 6 target BTEX compounds showed good linearity from 1-1000 ppm. The relative response factors for each compound were calculated relative to the internal standard. The relative standard deviations (RSDs) obtained from six determinations of RRF were under 3.5% (Table 2), this clearly demonstrated the statistictory reproducibility of the instrument performance. In order to avoid any possible loss of volatile VOCs because of time or concentration, all solution samples were directly weighed and extracted by n-hexane .Calibration curves for each of the BTEX compounds were obtained by plotting the relative response factor versus concentration. Limits of detection were obtained by immersing clean extraction media in successively dilute solutions of the individual BTEX compounds in amine or glycol until the corresponding signal of the BTEX compounds measured 2 x noise. Calibration curves for the BTEX compounds and a sample chromatogram can be seen in Figures 1 and 2 respectively. Finally, this method was tested and evaluated on real samples.

Table 2. GC output and calculated BTEX data of different samples.

| | 130ppm1-1 | | out of calculation | |
|-----------------------------|-----------|--------|--------------------|---------|
| | GC output | Calc | real amount | error % |
| Bz | 85.52 | 75.33 | 84.77 | |
| To | 23.21 | 21.56 | 24.68 | |
| Ebz | 11.60 | 10.77 | 11.95 | |
| o-Xy | 5.66 | 5.26 | 5.90 | |
| total | | 112.92 | 127.30 | -11.30 |
| corection factor | 0.93 | | | |
| corection for Bz of solvent | 4.1ppm | | | |

| | 130ppm1-2 | | | |
|-----------------------------|-----------|--------|-------------|---------|
| | GC output | Calc | real amount | error % |
| Bz | 98.07 | 86.99 | 84.77 | |
| To | 27.86 | 25.88 | 24.68 | |
| Ebz | 13.02 | 12.09 | 11.95 | |
| o-Xy | 7.03 | 6.53 | 5.90 | |
| total | | 131.48 | 127.30 | 3.29 |
| corection factor | 0.93 | | | |
| corection for Bz of solvent | 4.1ppm | | | |

| | 130ppm2-1 | | | |
|-------|-----------|--------|-------------|---------|
| | GC output | Calc | real amount | error % |
| Bz | 92.69 | 83.07 | 84.77 | |
| To | 26.05 | 24.49 | 24.68 | |
| Ebz | 13.31 | 12.51 | 11.95 | |
| o-Xy | 6.64 | 6.24 | 5.90 | |
| total | | 126.31 | 127.30 | -0.77 |

corection factor 0.94
 corection for Bz of solvent 4.1ppm

| 130ppm2-2 | | | | |
|-----------------------------|-----------|---------------|---------------|--------------|
| | GC output | Calc | real amount | error % |
| Bz | 89.05 | 79.64 | 84.77 | |
| To | 24.45 | 22.99 | 24.68 | |
| Ebz | 12.39 | 11.65 | 11.95 | |
| o-Xy | 6.25 | 5.88 | 5.90 | |
| total | | 120.16 | 127.30 | -5.61 |
| corection factor | 0.94 | | | |
| corection for Bz of solvent | 4.1ppm | | | |

| | mean value | error of mean value % | standard deviation |
|--------------|---------------|-----------------------|--------------------|
| Bz | 83.23 | -1.81 | 3.67 |
| To | 24.45 | -0.92 | 1.44 |
| Ebz | 12.09 | 1.13 | 0.43 |
| o-Xy | 6.22 | 5.34 | 0.33 |
| total | 125.99 | -1.03 | 5.67 |

| 285ppm1-1 | | | | |
|-----------------------------|-----------|---------------|---------------|-------------|
| | GC output | Calc | real amount | error % |
| Bz | 188.86 | 197.17 | 189.80 | |
| To | 53.24 | 56.74 | 55.27 | |
| Ebz | 26.02 | 27.73 | 26.76 | |
| o-Xy | 12.55 | 13.37 | 13.20 | |
| total | | 295.01 | 285.03 | 3.50 |
| corection factor | 1.07 | | | |
| corection for Bz of solvent | 4.10 | | | |

| 285ppm1-2 | | | | |
|-----------------------------|-----------|---------------|---------------|--------------|
| | GC output | Calc | real amount | error % |
| Bz | 174.81 | 182.19 | 189.80 | |
| To | 48.90 | 52.11 | 55.27 | |
| Ebz | 23.84 | 25.41 | 26.76 | |
| o-Xy | 11.59 | 12.35 | 13.20 | |
| total | | 272.07 | 285.03 | -4.55 |
| corection factor | 1.07 | | | |
| corection for Bz of solvent | 4.10 | | | |

| 285ppm2-1 | | | | |
|------------------|-----------|---------------|---------------|-------------|
| | GC output | Calc | real amount | error % |
| Bz | 210.78 | 191.84 | 189.80 | |
| To | 59.57 | 55.37 | 55.27 | |
| Ebz | 28.98 | 26.94 | 26.76 | |
| o-Xy | 14.23 | 13.23 | 13.20 | |
| total | | 287.38 | 285.03 | 0.82 |
| corection factor | 0.93 | | | |

corection for Bz of solvent 4.10

| | 285ppm2-2 | | | |
|-----------------------------|--------------|--------|--------------|---------|
| | GC output | Calc | rreal amount | error % |
| Bz | 209.85 | 190.98 | 189.80 | |
| To | 59.39 | 55.21 | 55.27 | |
| Ebz | 28.95 | 26.91 | 26.76 | |
| o-Xy | 14.12 | 13.13 | 13.20 | |
| total | | 286.23 | 285.03 | 0.42 |
| corection factor | 0.93 | | | |
| corection for Bz of solvent | 4.10 | | | |

| | mean value | error of mean value % | standard deviation |
|-------|------------|-----------------------|--------------------|
| Bz | 190.55 | 0.39 | 6.20 |
| To | 54.86 | -0.74 | 1.96 |
| Ebz | 26.75 | -0.05 | 0.97 |
| o-Xy | 13.02 | -1.36 | 0.45 |
| total | 285.17 | 0.05 | 9.57 |

Conclusion

The enhancement afforded by the extraction medium allows limits of detection in the 1-4ppm range and results in increases of 2-3 orders of magnitude when compared to conventional solvent detection. Linear dynamic ranges of calibration are 1-2 orders of magnitude. Preliminary experiments on the application of the new method to real samples have shown promising results.

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