MONITORING OF PRINCIPAL INDUSTRIAL POLLUTANTS USING ENVIRONMENTAL MONITORING STATION

Javed A. Ansari[1]

1:Advisor, Environmental & Industrial Hygiene, Sabic Technology Center, Jubail

E-mail: ansarija@sabic.com

ABSTRACT

Source monitoring of Principal Industrial Pollutants namely NOx, SOx, CO, Hydrocarbons etc. following US-EPA's manual methods has not only labor and time intensive but also requires good skill and experience as these methods are more prone to human errors. Automatic monitoring systems are therefore more popular for such type of monitoring. Though some companies do possess automatic monitoring systems, Sabic's new Environmental Monitoring Station is hitherto unique in the kingdom with a view it is equipped with both ambient and sources monitoring devices for the major industrial pollutants. Among different emission monitoring philosophies, extractive-dilution sampling is contemplated to be simple, efficient and versatile means to provide continuous monitoring from the stationary combustion sources even in the most severe sampling situations.

This paper discusses the technical evaluation of different sampling methods with special emphasis on extractive-dilution sampling and the functioning of a dilution probe controller vis-à-vis dynamic gas calibrator to rationalize the performance. The paper also presents a performance evaluation study, of mobile station against conventional manual sampling and chemical methods, being conducted at one of the affiliate to validate the sampling protocol and to enhance confidence in the system.

Keywords: *Source emission, Dilution probe, Extractive sampling, Dry /Wet standard basis, Emission rate, F factor, Critical orifice, High performance venturi.*

الملخص

قياس الملوثات الصناعية والتي تتمثل غالبا من اكاسيد النيتروجين والكبريت و أول أكسيد الكربون وكذلك الانبعاثات الهيدروكربونية عن طريق الوسائل اليدوية والمخبرية والمعتمدة من منظمة حماية البيئة الأمريكية لا تتطلب الجهد والوقت فقط وإنما تتطلب مهارة عالية وخبرة طويلة في هذا المجال. وفي اغلب الأحيان تكون عرضة للأخطاء البشرية الغير مقصودة أثناء عملية القياس والتحليل والتي تؤثر على النتائج النهائية للقياسات. ولتفادي هذه المشاكل تعتبر أنظمة القياس الآلية هي السبيل الوحيد للحصول على نتائج لا تتأثر بالأخطاء البشرية الغير مقصودة ولا تتطلب الجهد والوقت والمهارة العالية كما في الطرق الاعتيادية.

وعلى الرغم من أن اغلب الشركات الصناعية الكبرى تمتلك هذه الأنظمة إلا أن الشركة السعودية للصناعات الأساسية (سابك) كان لها السبق في امتلاك نظام القياسات الذي يخولها من قياس الملوثات الصناعية في الهواء أو من مصادر انبعاثها مباشرة وكذلك قياس تغيرات الأرصاد الجوية. وعلى الرغم من اختلاف الفلسفة في قياس الانبعاثات إلا أن استخلاص العينات وإحلالها يعد من أدق واكفىء القياسات المستمرة للغازات أنفة الذكر والمنبعثة من مصادر الاحتراق

<div dir="rtl">

وذلك حتى في أصعب ظروف القياسا ت. تعرض هذه الدراسة التقييم الفني للعديد من طرق القياسات المختلفة والمستخدمة في قياس الإنبعاثات الصناعية والتركيز على طريقة الاستخلاص والإحلال وكيفية عمل منظم الإحلال وجها لوجه وكذلك معا ير الغاز الديناميكي في تقليل الجهد المطلوب في القياس. وكذلك تعرض هذه الورقة دراسة تعقيمية لعمل الأنظمة الآلية مقارنة بالوسائل اليدوية والمخبرية المستخدمة في القياس وهذه الدراسة أجريت في إحدى شركات سابك وذلك لتأكد من عمل هذا النظام وتعزيز الثقة في نتائج هذا النظام.

</div>

1.   INTRODUCTION

In pursuit of SABIC's Corporate Environmental Mission to operate all its plants and ancillary units in total compliance with applicable regulations, the Environmental & Industrial Hygiene Group of (STC-J) is continuously developing in-house capabilities. SABIC Technology Center Jubail is fully committed to provide comprehensive environmental support and highly specialized services to all SABIC affiliates to meet their environmental compliance challenges. Environmental Monitoring Station (EMS) is a recent addition to its capabilities in the area of ambient and stacks emission monitoring.

SABIC's Monitoring Station has been specifically tailored for measuring criteria pollutants from both ambient and stationary combustion sources even in the most severe sampling situations. It could also be utilized to evaluate the need of Continuous Emission Monitoring System (CEMS). Prior to this automated system, SABIC's environmental group was conducting manual sampling for NOx and SO_2 and analyzing the collected sample by wet chemical methods.

2.   ENVIRONMENTAL MONITORING SYSTEM DESCRIPTION

The EMS housed highly sensitive and precise analytical instruments capable of analyzing pollutants in ppb levels. It is also configured with full range of meteorological censors that validate the air quality data. The monitoring station is operated through a computer using Station Manager software that offers many advanced features and capabilities including total control over the analytical instruments and meteorological monitoring network. The Monitoring station can be remotely connected, from the office, dialing out through the modem and telephone line to access and control the Station Manager to perform remote operations including auto calibration. The monitoring station incorporates the following analytical instruments together with span-gas calibrators and meteorological censors.

2.1 Analytical instruments and calibrators

The EMS is configured with the following range of analyzers for criteria pollutants. Ozone, carbon monoxide and methane/non-methane analyzers are used as stand-alone. However, NOx analyzer is used for multi analyses like NO, NO_2, total Nitrogen (Nt) and NH_3 after employing appropriate channels and converters. Similarly, SO_2 analyzer is used for H_2S measurement as well when used in combination with the H_2S converter unit. There are two calibrators used for generating dilution standards for calibrating these analyzers. Dynamic gas calibrator is used in ambient mode while dilution probe controller is used in conjunction with dilution probe in source monitoring mode.

2.2 Meteorological censors and other accessories

Meteorological censors include temperature, barometric pressure, wind speed, wind direction, rain gauge, and relative humidity. Met One Instruments, USA, manufactured all these censors. Other accessories comprise high volume air sampler for particulate matters (PM10) in the ambient air, hydrogen generator, zero air generator, air purification system, and 16-channel data logger, operating and control software etc.

3. SOURCE SAMPLING TECHNIQUES

Various techniques are used to sample the stacks emission that is subsequently measured either by wet chemical methods or by on-line analyzers. The selection of these monitoring techniques depends on characteristics of flue gas, moisture contents, and ingress to the sample port together with economic justifications. Some of the important monitoring techniques are,

- In situ point
- In situ cross- stack
- Extractive-direct
- Extractive –dilution

In-situ point: An in-situ type of sampling system, the measurement probe is inserted into flue gas. The gas is measured over a cell of small length located at the end of the probe. UV usually measures sample or IR based analyzers.

In-situ cross-check: Transmitter and receiver are installed on opposite site of the stack. The sample is subsequently measured by UV or IR based analyzers.

Though these monitoring systems are multi components and low selling price but needs heavy supporting frames and high installation costs. The disadvantages of such system include limited stack temperature, water vapor cross interference, indirect calibration, non-accessible location for high skill maintenance.

Extractive-direct system: The sample is taken from the stack with a probe and is transported to the analyzer housing. The heated transfer lines are used to prevent the moisture from condensing in the sample line. The concentration of analytes soluble in water is slightly affected as the moisture is knocked out before entering in to the analyzer. The measurement is made on dry basis and not affected by changes in the flue gas temperature, pressure or particles. However, the sample treatment is quite complicated and sample is less representative.

Extractive-dilution system: It is a unique extractive gas sampling system with in-situ sample conditioning performed at the probe tip by diluting a sample of the filtered stack gases drawn through a critical orifice with dry instrument air. This unique method of sample conditioning in the probe tip lowers the dew point of the sample to a temperature below the extreme ambient temperature at the installation thereby eliminates the need for heated transfer lines. Since moisture has not been removed from the sample, the measurement is on a wet standard basis -- the EPA's preferred method. This diluted sample is then transported under pressure through the sample line to the selected instrument. Thus providing reliable measurement with high accuracy and freedom from interferences.

Advantages of Dilution Probe System

- Sample dilution eliminates condensate problems and the need of heated sample lines.
- Sample is measured on standard wet bases, an EPA preferred method.
- No limitation on stack temperature and pressure.
- Monitoring is time and labor effective.
- Analyzers are intrinsically protected from any water condensate.
- Low-level measurement due to diluted sample, no risk of signal saturation.
- Long filter life due to clean sample and low sampling rate.
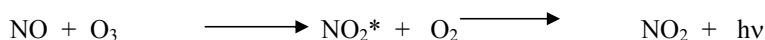
Disadvantages of Dilution Probe System

- Less representative sample due to dilution.
- Low range analyzers are expensive and one analyzer per measurement.
- Dilution calibration checks are is required to ensure constant dilution ratio throughout the measurement.

4. MEASURING PRINCIPLE

All the above analyzers and calibrators are designed to meet or exceed the US-EPA requirements using advance technology and most are accredited by US-EPA. A brief description focused only on operating principle and mechanism of some of the selected/critical instruments is given below for better understanding.

4.1 Chemiluminescence NH_3-NO/NO_2/NOx analyzer

The Chemiluminescence based analyzers are capable to measuring oxides of nitrogen from parts per billion (ppb) to 100 parts per million (ppm). The sample being analyzed is blended with ozone in a flow reactor. The reaction produces Chemiluminescence with intensity proportional to the concentration of NO. Specifically light emission results when electronically excited NO_2 molecules represented by NO_2* decays to lower energy states. A photo multiplier tube detects the light emission, which in turn generate proportional electronic signal.

$$NO + O_3 \longrightarrow NO_2^* + O_2 \longrightarrow NO_2 + h\nu$$

To measure the NOx (NO + NO_2) concentration, NO_2 is transformed to NO prior to reaching the reaction chamber. The resulting signal represents the NOx concentration. Similarly, NO_2 and NH_3 are transformed into NO using heated converter that combines with original NO in the reaction chamber. The resulting signal represents the total nitrogen. Ammonia concentration is determined by subtracting the signal obtained in the NOx mode from the signal obtained in the total nitrogen (Nt) mode.

Dynamic gas calibrator

The dynamic gas calibrator supplies precise levels of standard calibration gases like ozone, carbon monoxide, sulfur dioxide, nitric oxide etc. The gas levels are used to calibrate instruments and perform zero and span checks, audits, and multipoint measurements. The instrument design meets all published US-EPA requirements for multipoint calibration, audit, level-1 span, and precision checks.

The model 146C of Thermo Environmental Inc. has four flow modules namely gas dilution, transfer standard ozone generation, gas phase titration, and permeation tube oven. These modules are used to generate dilution standard, ozone transfer standard, and NO_2 standard through gas phase titration and permeation tube oven. The Figure-1 schematically represents the flow through each module. In all cases, the flows are set using mass flow controllers.

Gas dilution is achieved by utilizing two or more mass flow controllers. One in a high flow controller (typically 10 slm full scale) to govern the diluting zero air. The other controller is for low flow (typically 100 sccm) and governs the flow of the gas to be diluted. A Teflon mixing chamber is used to achieve complete mixing of the two components.

Dilution probe mechanism: The dilution probe controller works in conjunction with different sonic orifice configurations for systems requiring various dilutions. There are four lines in the dilution probe assembly namely, dilution air, calibration line, diluted sample and a vacuum line. The dilution air delivers high pressure zero air to the probe, which is used for sample dilution. The calibration line is used to deliver either zero air or span gas to the probe.

The dilution probe controller selects the zero air or span gas or the sample to mix with the high pressure zero air. A high performance venture allows the critical orifice to draw the sample and mixed with dilution air in the mixing chamber. The diluted sample is then transported through the sample line under positive pressure to the analyzer housing for the measurement. The device is specifically designed to measure stack effluents by mixing the exhaust gases with high pressure regulated zero air at a known dilution ratio. A critical sonic orifice draws the span gas that flows through the calibration line to the probe. The probe schematics are shown in the Figure-2.
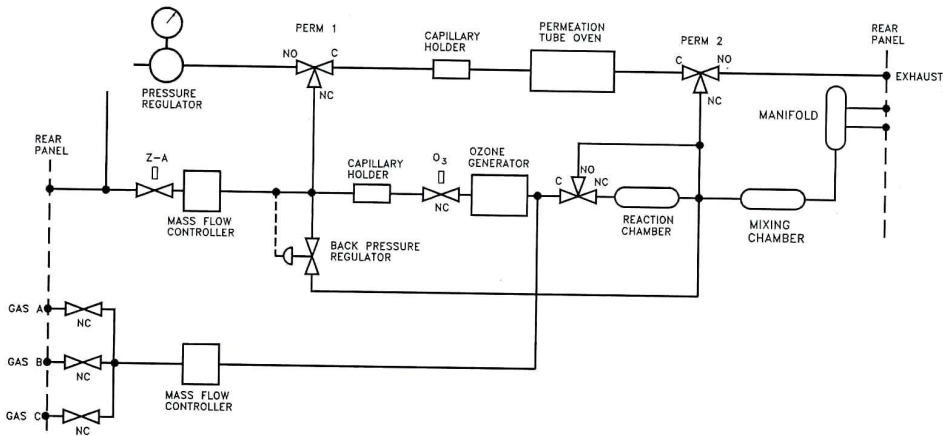

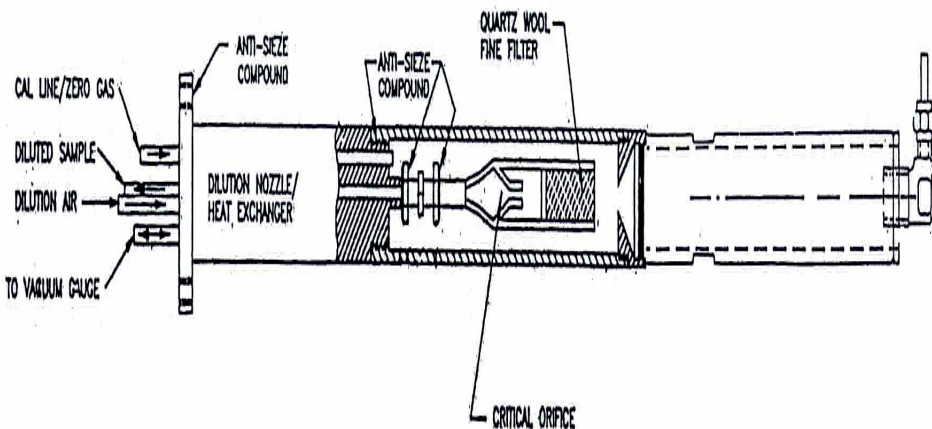Figure-1   Schematics of Multi Gas Calibrator

Figure-2   Schematics of Dilution Probe

Dilution probe controller regulates the flow of dilution air to the probe, diluted sample to the analyzer, monitors the vacuum generated by the aspirator in the probe tip and also controls the flow of the calibration gases for a truly dynamic calibration.

5. MEASUREMENT SYSTEM PERFORMANCE TEST PROCEDURE

The main objective of the study was to verify the sampling protocol and calibrator's performance. A crosscheck study is therefore initiated to verify the results of monitoring station with that of equivalent US-EPA manual methods to establish the confidence. The sampling was conducted on Utility Boiler at one of the SABIC affiliate by both on-line measurement and manual sampling techniques. Since manual sampling and chemical analysis procedures as outlined in the Method-6 and 7 of US-EPA CFR 40 PART 60 are extremely time and labor intensive, the monitoring was limited to NOx measurement only using US EPA's Method-7 & 7e for this crosscheck study.

As the monitoring results are highly influenced by instrument calibration, a crosscheck study was conducted to evaluate the performance of the two calibrators against each other using standard calibration blend. Different dilution standards were prepared using dynamic gas calibrator and checked on an pre-calibrated analyzer. Since the intent is to verify the dilution mechanism and the accuracy of both the calibrators, the highly precise NOx analyzer is selected for this study. The results of the study demonstrate excellent agreement having 2.53% relative error between the two calibrators. The data derived from prepared dilutions from the base 87-ppm standard blend and their subsequent measurement on NOx analyzer is summarized in Table-1 to demonstrate the agreements between them.

Table-1: Performance of Dynamic Gas Calibrator Versus Dilution Probe Controller

NOx Standard	Dynamic Gas Calibrator			Dil. Probe Controller		% Error
	Dynamic Calibrator	Analyzer Reading	% Error	Dil. Probe Controller	Analyzer Reading	Ambient v/s Source
87 ppm	0.44	0.436	1.82			
	0.87	0.856	1.61	100 X	0.892	2.53
	1.60	1.589	0.7			
	2.00	2.017	0.85			

6. PROCEDURE

Samples were extracted from the stack using both manual and automatic sampling techniques following standard methodology. Samples collected in the absorbing solution were analyzed in the laboratory on a calibrated spectrophotometer. However, in the instrumental analysis, all

the analyzers were calibrated using standard gaseous blends in the sample concentration range. The stack sample was diluted in a special probe and transported to the analyzers where it was analyzed instantaneously. The details of both sampling procedures were discussed below.

6.1 Manual chemical method

The stack sampling and chemical analysis were conducted by adopting method seven [US-EPA, 1995]. The sample was extracted using heated sampling probe from the stack into an evacuated 2-L round bottom flask containing 25 ml of absorbing solution. The temperature, barometric pressure, vacuum, etc were taken during sample collection and volume sampled was corrected to the real parameters. The sampling train used for the NOx is shown in Figure-3.
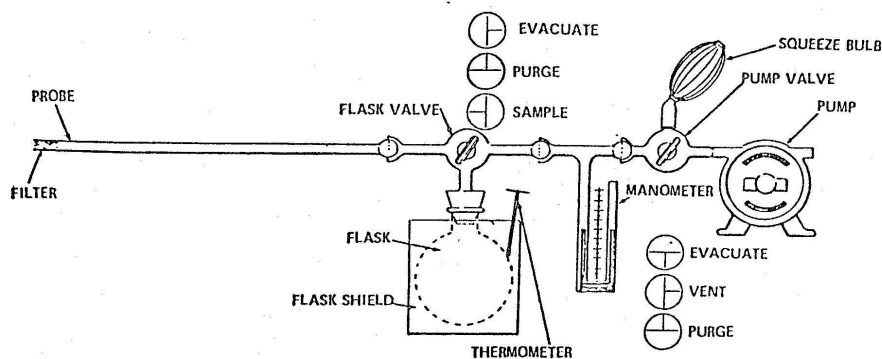

Figure-3 NOx Sampling Train

Sample Recovery: After a reaction time of 16 hours, the temperature and pressure of the flask is recorded. The absorbing solution of the flask is then transferred into a pre-labeled polyethylene bottle. The flask was rinsed twice with 5 ml portion of deionized water and the rinsed water is added into the sample bottle. Finally the sample pH is adjusted between 9-12 using (1N) caustic solution.

Sample Analysis: The recovered samples along with reagent blank were sent to the independent commercial laboratory (Inspectorate Watson and Gray Ltd.) for analysis. Colorimetric, Phenol disulfonic Acid (PDS), method [ASTM, 1998] is used to measure nitrogen oxides (NOx) except nitrous oxide (N_2O). The color intensity is measured at a wavelength of 406 nm using quartz cell of one-inch optical path length. The applicable range of this method has been determined to be 2 to 400 mg NO_x, expressed as NO_2 per dry standards cubic meter without having to dilute the sample. Higher concentrations of NOx may

be measured following suitable dilutions.   Reagent blank and other QC checks were made during the analysis to assure accuracy of the analytical results.

6.2   Automated instrument method

The Environmental Monitoring Station is used to measure on-line stack pollutants [US-EPA, 1995]. The dilution probe is subjected downstream into the stack sampling port. The probe is suitable even in the applications with high temperature (up to 1100 ^{o}F) or very high opacity, offers extractive gas monitoring with in-situ sample conditioning. The long insulated Teflon sampling lines are connected to the probe at the stack and leak checks were assured. The monitoring system was then switched over to source mode to collect the actual stack sample. All the analyzers were first calibrated using zero and span gases. After the calibration, the diluted stack sample is continually fed to analyzers where it is analyzed and instantaneous results are displayed at the panel and also recorded in the database.

7.   QUALITY ASSURANCE

All the analyzers were calibrated with working standards prepared from dynamic gas calibrator having precise mass flow controllers from the certified gaseous blend in the same range as that of sample concentration before measuring the actual stream. The performance of dilution probe was checked on these calibrated analyzers. Calibrations were rechecked between each sample run to assure analyzer's integrity in line with requirements.

8.   CALCULATIONS

Results are obtained in terms of ppm from wet chemical method or directly from on-line analyzer that are subsequently converted in to standard energy unit i.e. nanogram per Joule of heat input. This is accomplished using the following equations-1&2 where emission rate largely depends on the excess air used in the combustion process and of course F factor [US-EPA, 1995], which relates to the type of fuel used.

Emission rate E (ng/J) = $[(C_w\,M)\,F_w\,20.9]$ / $[20.9\,(1-B_{wa}) - \%O_{2\,w}]$ ………………… (1)

Emission rate E (ng/J) = $[(C_w\,M)\,F_d\,20.9]$ / $20.9\,(1-B_{ws}) - \%O_{2\,w}]$ ……………….. (2)

Where

$\quad$ C_w $\qquad$ Concentration of pollutant in ppm on wet basis.

$\quad$ M $\quad$ Factor for the conversion of ppm results into mg/scm at standards conditions   and 10^6 is multiplier to change mg into nanogram. It is 1.912 for NOx and 2.66 for SO_2.

$\quad$ % O_{2w} $\quad$ Oxygen contents in the flue gas on wet basis.

F_w Represents the ratio of the gas volume of the combustion products to the heat contents of the fuel used. This is 2.85 x10^{-7} for natural gas and 2.77 x10^{-7} for liquid fuel.

F_d Represents the ratio of the gas volume of the combustion products to the heat contents of the fuel used. This is 2.43 x10^{-7} for natural gas and 2.47 x10^{-7} for liquid fuel.

B_{wa} Moisture fraction of ambient air, usually 0.025

B_{ws} Moisture fraction of effluent gas

Example Calculation: The NOx emitting from Utility Boiler is found to be128.9 ppm and excess oxygen was 3.8 % at the time of measurement. The boiler is using natural gas. Then by substituting the data in the above equation-1,

$$\mathbf{E} = 128.9 \times 1.912 \times 10^6 \times 2.85 \times 10^{-7} \times 20.9 / \{(20.9\text{-}0.025) - 3.8\} = \mathbf{88.4 \ ng/j}$$

Similar calculations were made to obtain SO_2 results in ng/J unit

9. RESULTS AND DISCUSSION

The results obtained from the Station Manager's database for NOx and SO_2 are shown in the Table-2. These concentrations together with excess oxygen were used to calculate the emission rates of nitrogen dioxides, and sulfur dioxide from the stack under evaluation. In this very case, the NOx emission (87.6 ng/J) is just above the applicable regulation, which is 86 ng/J for the boilers firing natural gas.

Table-2: NOx and SOx Results Using EMS

Time Hours	NOx		SO$_2$		% O$_2$
	ppm	ng/j	ppm	ng/j	
11:40	128.9	88.4	5.4	5.2	3.8
11:48	126.5	88.9	4.8	4.7	4.2
11:52	125.6	87.7	4.6	4.5	4.1
11:59	123.7	85.5	3.2	3.1	4.0
Average	126.2	87.6	4.5	4.4	4.0

The following Tables-3 displays the results reported through manual sampling and wet chemical analysis. The concentration values are then converted into standard energy unit in accordance with US EPA method-7.

Table-3 : NOx Results Using Manual Chemical Method

Time	O₂	NOx	
Hours	%	ppm wet basis	ng/j
14:15	4.3	126.8	89.6
14:30	4.2	123.4	86.7
Average	4.25	125.1	88.1

The results presented in the Tables-2 and 3 correspond to the two different techniques that were utilized for crosscheck study, which demonstrates good correlation. The analytical results of manual sampling show that some flasks have the vacuum leakage before sampling itself as low values are obtained from those flasks. These data were not considered valid for the intended study. The results of monitoring station, however, are exceptionally precise and accurate covering long time interval thus present the long time average concentration of the pollutants.

The results obtained in ppm were converted into milligrams per cubic meter that are used to calculate the emission rate in terms of standard energy unit i.e. nanograms per joule of heat input (ng/j), by adopting standard conversion formula. The precision of results obtained through manual technique largely depends on the skill and experience of the personnel and careful execution of sampling procedures as human error is of paramount importance. However, human error is minimized in automatic sampling and on-line determination of analyte. Problem of water condensation is most common which is eliminated in the specially designed dilution probe methodology that brings the moisture down to a level were it remains suspended in diluted sample. Since the EMS is a continuous system, the results would also show certain pattern if contributing streams undergo certain decoking or regeneration phase during a continuous operation.

10. CONCLUSION

The calibration of all the analyzers using dynamic gas calibrator and the verification of the dilution ratio accomplished by dilution probe demonstrate the reliability of data obtained through automatic source monitoring system. These data have been further crosschecked against the data   obtained by manual sampling technique. The excellent agreement between the results obtained by two different techniques proves the quality of monitoring data.

The emission monitoring study carried out on a utility boiler at one of SABIC affiliate reveals total compliance for SO_2 with applicable standards as sulfur free fuel is used. The NOx results obtained by manual method was found to be 125.1 ppm equivalent to 88.1 ng/J. It is however measured 126.2 ppm equivalent to 87.6 ng/J by automatic monitoring system. Though NOx

was found slightly above the regulated limit, nevertheless these data show high degree of agreement that demonstrates the validity of EMS in source monitoring applications. Furthermore, the EMS provides following added advantages.

- Ability to measure Destruction Removal Efficiency (DRE) of incinerators using methane/ non-methane analyzer.

- Ability to measure criteria pollutants in both ambient and source mode.

- Ability to monitor continuous emission (CEMS) from any combustion source.

- Dilution probe eliminates condensate problems and the need of heated sample lines.

- Sample is measured on standard wet bases, an EPA preferred method.

- Time and labor effective.

In view of above validation study, it is believed that SABIC's new Environmental Monitoring Station offers a simple, efficient and versatile means to monitor the principal industrial pollutants emission from the stationary combustion sources even in the hostile sampling situations. Due to strict regulations, it is being heavily used in other affiliates. The automated system offers real time data of all the analytes in a single run that has enabled SABIC to provide prompt support and services to all affiliates. This would, otherwise, have been very time and labor-intensive using manual sampling and chemical analysis methods for each analyte monitoring.

REFERENCES:

1. ASTM Standards, 1998, Part-26, D 1608-60, Philadelphia, PA, USA.

2. Code of Federal Regulations, 1995, US-EPA, CFR40, PART 60, Method-7, The Office of the Federal Register, NARC, USA

3. Code of Federal Regulations, 1995, US-EPA, CFR40, PART 60, Method-7e, The Office of the Federal Register, NARC, USA

4. Code of Federal Regulations, 1995, US-EPA, CFR40, PART 60, Method-19, App. A, The Office of the Federal Register, NARC, USA