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DETERMINATION OF THE MASS CONCENTRATION OF NITROGEN OXIDES IN THE WORK PLACE AIR BY CHEMILUMINESCENCE METHOD

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Abstract. *A rapid, senstive method for NO_2 analysis utilizing the chemiluminescence reaction of NO and O_3 is provided by the use of the Scott Model 125 Chemiluminescense NO/NO_I, Analyzer.*

Measurement of NO_2 in the air sample by reducing it to NO by passage tgrough a converter before it enters the reaction chamber. Thermal converter will also convert, partially or completly, NH_3 (and other N-componds) depending on converter type and temperature.

In the air at many work places in the fertilizer factory, NH_3 and NO_2 may be present simultaneously and NH_3 may cause interference when NO_2 determine by this method. The aim of this study was to determine the influence of the converter temperature to the conversion of NO_2 and NH_3 to NO.

1. OPERATION

The principles of operation is based upon the NO/O_3 chemiluminescent reactions in wich O_3 react with O3 react with NO to yield O_2 and electronically exicited NO_2. The transition of excited NO_2 to graund state NO_2 yields a detectable light emission. This light emission is then measured using a photomultiplier and associated electronic.

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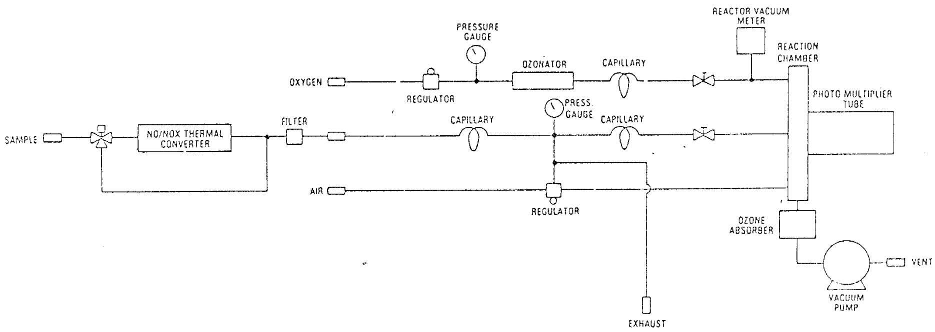

Fig. 1. Flow diagram

2. DETERMINATION NO CONCENTRATION

The method allso utilizes the principle that thermal decomposition of NO_2 is complete at about 540°C (1100°F). Alenght of coiled seamless stainless steel tubing heated, using a low voltage, high current power supply, to a temperature od 700°C (1300°F) provides sufficient residence time at a sample flow rate of 10 scfh for essentialy complete conversion of NO_2 to NO.

a) Analyzer unconverted NO_x (bypass converter) and record the true level ofNO indicated on the readout meter.
b) Divert NO_x throught the Thermal Converter (changes NO_x to the total NO), then direct to the analyzer. Record the level of total NO indicated on the readout meter.
c) The difference in the level of total NO and true NO becomes the calculated level of NO_2 in the sample gas.

In the fertilizers factory there is a constant control of the working area pollution by measuring NO_2, NH_3, dust, etc. concentrations.

The presence of NH_3 in the working area makes it difficult to determine NO_2 by chemiluminescence method because at high temperatures of the converter NH_3, itself, is partially converted into NO.

This distrubance caused by ammonia is especially emphasized when very low ppm concentrations of NO_2 are to be determined. (MAC of NO_2 in the working area is 1 ppm).

The objective of this paper is to examine the possibility of measuring NO_2 at lower working temperatures of the converter when the influence of NH_3 would be reduced or totally eliminated.

For this puprpse some calibration mixtures were prepared with different concentrations of NO_2, i.e. NH_3 into the air, and conversion level of NO_2 i.e. NH_3 was determined at 6 different converter temperatures.

A permeation tube EL-SRT-2 (KIN-TEK Laboratories Inc.) was used for the preparation of these calibration mixtures of NO_2. The same tube was used for the calibration mixtyures of 5.5 ppm and 11 ppm NH_3. The mixtures with higher concentrations were obtained by blending the instrument air and pure NH_3 in Teflon bags of 501. The results are given as diagrams and as tables.

Table 1.

Calibration mixture	1 ppm NO_2		1,5 ppm NO_2		3 ppm NO_2		6 ppm NO_2		12 ppm NO_2	
Convertor t°C	a	b	a	b	a	b	a	b	a	b
700	0.96	100	1.47	100	2.90	100	6.10	100	12.10	100
650	0.57	59.40	1.21	82.30	2.47	85.20	5.50	90.15	11.20	92.60
600	0.39	40.60	0.96	65.30	1.78	61.40	4.60	75.40	10.00	82.60
550	0.23	24.00	0.74	50.30	1.45	50.00	3.60	59.00	8.50	70.25
500	0.16	16.70	0.62	42.20	1.30	44.80	2.90	47.50	7.45	61.60
400	0.13	13.50	0.55	37.40	1.15	39.70	2.25	36.90	5.60	46.30

a-NO_2 concentration (ppm)
b-conversion level NO_2 to NO (%)

Table 2.

Calibration mixture	1 ppm NO_2		1,5 ppm NO_2		3 ppm NO_2		6 ppm NO_2		12 ppm NO_2	
Convertor t°C	a	b	a	b	a	b	a	b	a	b
700	3.00	54.55	2.10	19.10	8.70	39.55	20.50	37.30	39.50	35.90
650			1.50	13.60	7.90	335.90	20.20	36.70	43.10	39.20
600	2.40	43.65	0.72	6.55	6.60	30.00	18.60	33.80	44.70	40.65
550			0.40	3.65	5.15	23.40	16.20	29.45	40.20	36.55
500	1.00	18.20	0.23	2.10	3.55	16.15	10.00	18.80	21.20	19.30
400			0.13	1.20	1.55	7.00	3.60	6.60	6.10	5.50

a-NO_2 concentration (ppm)
b-conversion level NH_3 to NO (%)

3. CONCLUSIONS

The conversion level for low NO_2 concentration to NO depends on the converter temperature and these analyses must be carried out at the converter operating temeperature (700°C), when the conversion level is 100%.

Gas mixtures containing higher concentration of NO_2 (<10 ppm) indicated to the less temperature dependance of the conversion level, and consequently, it would be, probably, possible to determine thesse concentrations by the temperatures below refered tot he rated converter temperature (700°C).

The conversion level of NH_3 to NO on the rated temperature (700°C) amounts 30% to 55% depending on ammonia concentration. The conversion level of various concentrations of ammonia into NO by the lower converter temperatures (bellow 500°C) is <15%, but on these temperatures the conversion of NO_2 into NO is not complete (between 40% and 55%).

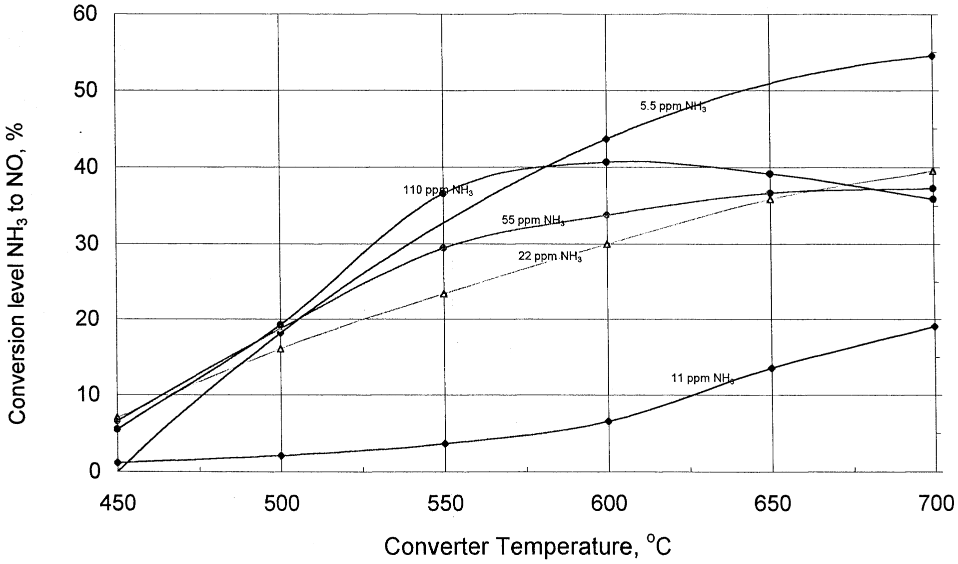

Fig. 2.

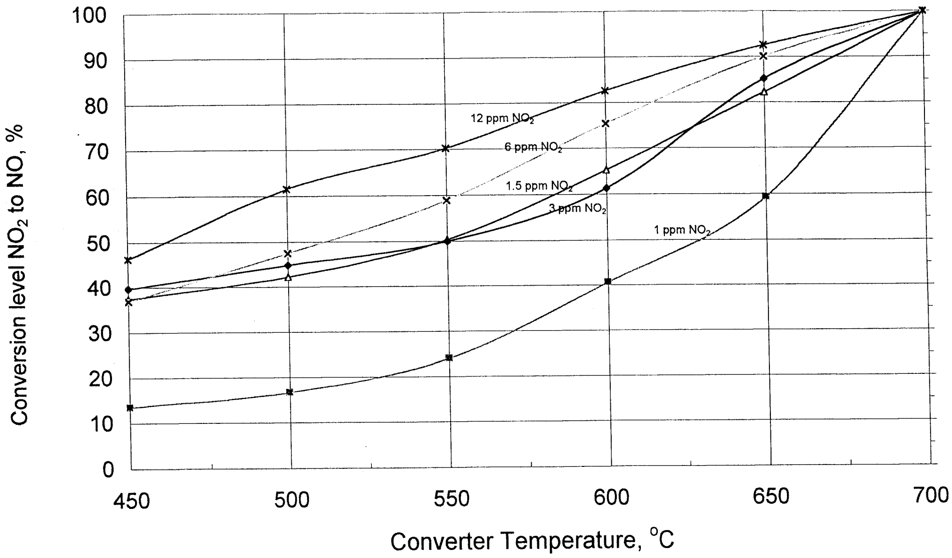

Fig. 3.

As follows, ammonia is partialy converted into NO, so it must be eliminated from the air sample, by passing the sample through 10% sulphuric acid.

Example 1

Sample gas contain:	Reading on read out meter
1.20 ppm, NO_2	1.20 ppm, NO_2
1.20 ppm, NO_2+15 ppm NH_3	1.70 ppm NO_2
After removal NH_3 by 10% H_2SO_4	1.25 ppm, NO_2

Example 2

Sample gas contain:	Reading on read out meter
3.50 ppm, NO_2	3.50 ppm, NO_2
3.50 ppm, NO_2+30 ppm NH_3	6.00 ppm NO_2
After removal NH_3 by 10% H_2SO_4	3.80 ppm, NO_2

ODREĐIVANJE MASENE KONCENTRACIJE AZOTNIH OKSIDA U ATMOSFERI RADNIH PROSTORA PRIMENOM HEMILUMINISCENTNE METODE

Ralević Gordana, Oravec Miroljub

Brz i osetljiv postupak određivanja sadržaja NO_x u gasovitim uzorcima postiže se primenom hemiluminiscentnog NO/NO_x analizera, Scott Model 125. Princip rada ovog analizera se zasniva na NO/O_3 hemiluminiscentnoj reakciji pri kojoj se formira elektronski eksitiran NO_2 koji prelaskom u osnovno stanje emituje svetlosnu energiju proporcionalnu količini NO u uzorku. Merenje koncentracije NO_2 u uzorku se vrši njegovom konverzijom u NO što se postiže prolaskom uzorka kroz termalni konvertor (t=700°C) a pre ulaska uzorka u reakcionu komoru. Termalni konvertor će konvertovati, delimično ili potpuno, zavisno od svoje temperature, NH_3 i dr. N - jedinjenja prisutna u uzorku. U fabrici za proizvodnju veštačkih đubriva "Azotara" vrši se konstantna kontrola zagađenosti radnih mesta na sadržaj NO_2, NH_3 prašine i dr. zagađivača. Prisustva NH_3 u atmosferi čini smetnju pri merenju koncentracije NO_2 primenom ove metode, pogotovo pri određivanju malih ppm-skih koncentracija NO_2. (MDK NO_2 za radno mesto je 1 ppm). Cilj rada je ispitati mogućnost merenja koncentracije NO_2 na nižim t°C konvertora (< 700°C) kada bi se uticaj NH_3 znatno umanjio ili potpuno eliminisao. Za ovu svrhu pravljene su kalibracione mešavine sa različitim koncentracijama NO_2 odnosno NH_3 u vazduhu (korišćene su permeacione cevčice) i stepen konverzije NO_2 odnosno NH_3 određivan je na 6 različitih temperatura konvertora. Eksperimentalni rezultati pokazali su da se na nižim temperaturama konvertora konvertora (< 700°C) konverzija NH_3 u NO znatno smanjuje ali istovremeno i konverzija NO_2 u NO na ni`im t°C nije kvantitativna tako da sledi da se merenje koncentracije NO_2 mora vršiti na radnoj t°C konvertora konvertora (700°C) a amonijak iz uzorka uklanjati prolaskom uzorka pre ulaska u analizer kroz ispiralicu sa 10% H_2SO_4.