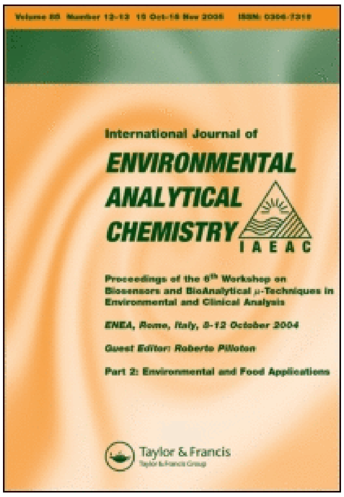

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Integrated Manual Method for Determination of Nitrogen Oxides in Source Effluents[†]

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A manual integrated method is described which utilizes an alkaline permanganate sampling train for the collection of nitrogen oxides from stationary sources. The total nitrates collected are determined by colorimetric procedure with 2,6-xylenol. Sample flow rate for maximum collection efficiency is 0.3 l/min or lower. Sampling time depends on the NO_x concentration expected and the variation of process conditions. Data is shown comparing the proposed method with the accepted one from several types of emission sources.

KEY WORDS: Nitrogen oxides, integrated sampling, emission sources, air pollution.

INTRODUCTION

Nitrogen oxides (NO_x) are one type of the air pollutants emitted from stationary sources such as combustions and industrial chemical processes. The test procedure for compliance and evaluation of stationary sources for NO_x is the method of the phenoldisulfonic acid procedure (PDSA), which was promulgated by EPA as reference method.[1] Sampling for only 15 sec., of course, does not provide a

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representative sampling of emissions, mainly as the NO_x concentrations in a stack can change in time due to the variation of process conditions, and, in practice, it is necessary to take numerous samples. In addition rapid analysis is not possible, however Guggenberger *et al.*[2] proposed a modified procedure which can be effected more quickly. The efficiency of grab sampling PDSA method decreases rapidly at low NO_x concentrations.[3]

It is evident that the NO_x sampling problems could be minimized if a reagent were available which would rapidly and quantitatively absorb NO_x in a gas stream. This would allow time-integrated sample collection and also provide a sample concentration technique which could result in precise analysis of any NO_x emission level. Several attempts have been made to develop a time-integrated sampling technique which are described in the literature.[4–8]

The present report describes the application of an integrated manual method which utilizes an alkaline permanganate absorption solution and an easy well-known analytical procedure for analysis of nitrates with xylenol. The results of the integrated manual method are comparable with the PDSA reference method. The work also involves sampling in real stacks and simulated atmospheres.

EXPERIMENTAL PROCEDURE

Sample collection

The sampling train corresponds with the absorption method recommended by USEPA for gaseous pollutants.[9] The sample collector consists of three impingers (300 ml) which have been modified by replacing orifice and impaction plate with a semi-fine frit 40–100 μm of porosity. 75 ml of absorption solution (4.0% $KMnO_4-2.0\%$ NaOH) was placed in each of the three modified impingers and silica gel to the fourth midget impinger. Optimum sample rates for maximum collection efficiency is described in the results. Sampling time depends on the NO_x concentration of the gas effluents and the process conditions.

Analysis

The nitrate content in samples has been successfully determined by the colorimetric method using 2,6-xylenol[10] with some necessary adaptations to the characteristics of the samples. Previously, the interference of permanganate excess had to be removed with oxalic acid. Working standards with KNO_3 are used to prepare a concentration versus absorbance curve and a blank should be run. The developed color is very stable and the plotting data present a good fit and also a good reproducibility. A detailed procedure is available from the authors.

RESULTS AND DISCUSSION

The collection efficiency and the total recovery of the absorption solution were determined by sampling known mixtures of nitric oxide in nitrogen atmosphere. Two kinds of concentrations were used: 101 and 920 ppm of NO from aluminium cylinders with certificated analysis. Both integrated manual and PDSA analysis results are given in Table I. The results show there is no significant difference between the two procedures.

TABLE I
Comparison of integrated manual method versus grab sampling (PDSA) method.

Sampling method	Sample concentration	Number of determinations performed	Mean concentrations $\bar{c}$ (ppm NO_x)	Standard deviation s (ppm)	Coefficient of variation CV (%)
Integrated manual[a]	101 ppm NO	4	105	1.1	1.0
Grab sampling (PDSA)	101 ppm NO	10	106	4.3	4.1
Integrated manual[b]	920 ppm NO	4	889	15.0	1.7
Grab sampling (PDSA)	920 ppm NO	19	949	32.8	3.5

[a] Sampling flow rate: 0.55 l/min. Sampling time: 60 minutes.
[b] Sampling flow rate: 0.19 l/min. Sampling time: 60 minutes.

Further laboratory experiments were carried out to determine the effect of sampling flow rates on collection efficiency. Data is shown in Table II and Figure 1. The results (Table II) indicate that the relation between collection efficiency and the flow rate is affected by the capture in the first impinger. Comparing the analytical recovery at different concentrations of NO we found that low concentrations

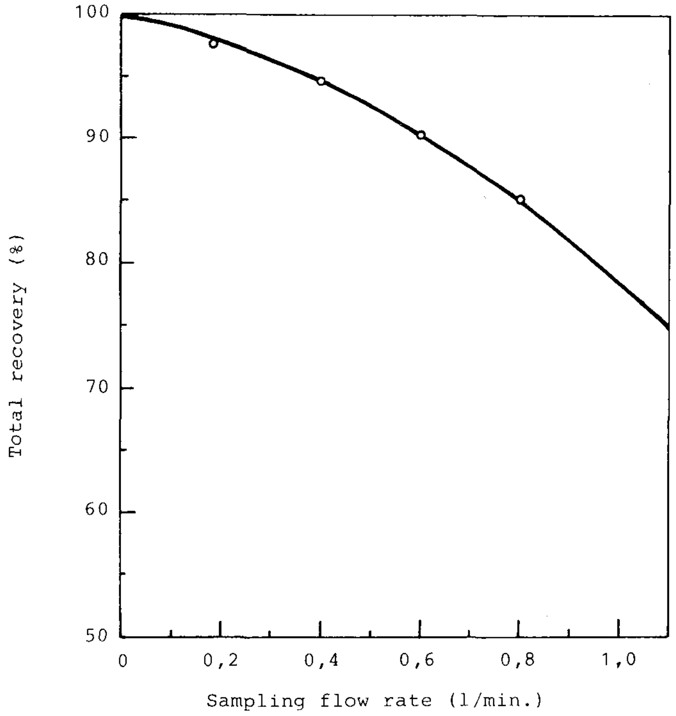

FIGURE 1 Effect of flow sampling rates in collection efficiency.

TABLE II
Collection efficiency and total recovery of sampling NO_x with 4% $KMnO_4$–2% NaOH

Experiment number	Number of determinations performed	Sample concentration NO (ppm)	Sample flow rate (l/min)	Collection efficiency (%) 1st impinger	Collection efficiency (%) 2nd impinger	Collection efficiency (%) 3rd impinger	Total recovery (%)
1	4	101	0.55	77.6	21.1	5.4	104.1
2	2	920	0.80	53.9	24.3	6.8	85.0
3	3	920	0.60	65.1	20.9	4.3	90.3
4	3	920	0.40	75.0	17.1	2.3	94.4
5	4	920	0.19	87.7	9.3	0.4	97.4

Sampling time: 60 minutes.

are less influenced by the flow rate, however high concentrations are more important. Thus, for maximum collection efficiency the flow rate should be maintained at 0.3 l/min or lower. On the other hand, the impinger temperature does not appear to have any effect on collection efficiency.

In Table III NO_x analytical results from several types of emission sources are compiled, comparing the integrated method with the accepted one (PDSA). It seems probable that the differences between both methods can be accounted for by the variations of the process conditions.

TABLE III
Field comparison results of integrated manual and PDSA methods

Source	NO_x (ppm) as NO_2	
	PDSA[a]	Integrated manual
Power plant steam generator (500 MW)[d]	687	623[b]
Power plant steam generator (300 MW)[d]	415	386[b]
Steam generator package boiler (40.10^6 BTU/h)[d,e]	84	78[c]
Steam generator package boiler (10.10^6 BTU/h)[d,e]	62	70[c]
Yellow mercuric oxide process[f]	1303[g]	781[h]
Nicotinic acid process[i]	1042	812[b]

[a] Mean of five samples.
[b] Mean of two samples at 0.19 l/min.
[c] Mean of two sample at 0.55 l/min.
[d] Natural gas as fuel.
[e] Modulated load.
[f] Production capacity: 400 kg of $Hg(NO_3)_2$ for cycle.
[g] Five samples distributed during the process time.
[h] Integrated sample throughout the process time.
[i] Nitration of β-picoline in three reactors of 1,600 gal.

CONCLUSIONS

The permanganate sampling method with analysis by colorimetric procedure with 2,6-xylenol is an easy manual method which offers a reliable way of obtaining an integrated measurement of nitrogen oxide emissions in stationary source effluents. Laboratory and field sampling present comparable results with the accepted one and it could be proposed as an alternative method to PDSA.

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