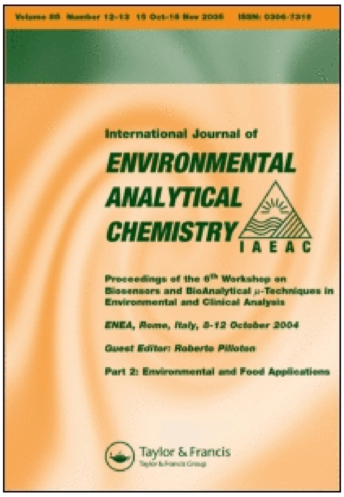

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

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To cite this Article Kosmus, W.(1985) 'Summation Method for Monitoring Nitrogen Oxides', International Journal of Environmental Analytical Chemistry, 22: 3, 269 — 279
To link to this Article: DOI: 10.1080/03067318508076426
URL: http://dx.doi.org/10.1080/03067318508076426

Intern. J. Environ. Anal. Chem., 1985, Vol. 22, pp. 269–279
0306-7319/85/2204-0269 $18.50/0

Printed in Great Britain

Summation Method for Monitoring Nitrogen Oxides†

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Dedicated to R. Pietsch on the occasion of his 60th birthday

(*Received December 17, 1984; in final form May 29, 1985*)

A simple method is described for monitoring nitrogen oxides over a period between one week and a month. The method is based on a piece of chromatographic paper, impregnated with diphenylamine, which is fixed onto a candle and exposed to the air. The nitrogen oxides in the air react with amine to form nitrosamine which is then extracted from the paper and determined by the usual laboratory methods. The results derived from this summation method correlate very well with those obtained from more sophisticated methods such as chemiluminescence.

KEY WORDS: Summation method, nitrogen oxides.

INTRODUCTION

In general, methods for monitoring air pollutants can be divided into three different groups. The first group uses sophisticated and therefore expensive instrumentation, in the second manual samples are obtained by purging air through a scrubbing solution, commonly referred to as "bubblers", the third group encompasses summation or

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†Presented at the 14th Annual Symposium on the Analytical Chemistry of Pollutants, Barcelona, November 22–24, 1984.

accumulation methods where a chemical system is exposed to the ambient air forming reaction products with the pollutants, which are determined in the laboratory afterwards.

In the past, most attention in air quality studies was directed towards the determination of concentrations of sulphur dioxide, mostly as a result of the existence of simple, inexpensive methods of monitoring this pollutant, including a summation method. So far, the summation method for SO_2, the so-called lead candle, in which lead dioxide reacts with SO_2 to form $PbSO_4$, is the only one for air pollution widely used in many countries. The importance of such a summation method has resulted in several nationally proposed standards.[1]

The aim of the present study was to develop a summation method for nitrogen oxides for the following reason: Since the emission of SO_2 is kept within definite limits in most industrial countries, the focus of air pollution control has changed markedly towards the investigation of nitrogen oxides, their dispersion, transformation and deposition in the biosphere and upper layers of the atmosphere.

Nitrogen oxides not only pose a threat to the ecosystem, but also create substances such as ozone which are more harmful, especially to the vegetation. The increasing problem of deforestation and total destruction of forests in parts of Europe has lead to pollution control strategies, including the reduction of harmful vehicle exhaust gases, the main source of NO_x pollution.

Various methods, including two proposed by the WHO,[2] are employed to determine the extent and severity of NO_x pollution existing in different regions. In one continuous measuring method carried out by means of apparatus based on the chemiluminescence of the reaction $NO+O_3$, NO_2 is converted to NO prior to measurement. This method has all the advantages necessary for such monitoring, sensitivity and accuracy, but has one disadvantage: it is quite expensive and relies upon a source of electric power. The high cost of a station limits their number, for example only 290 stations are planned for the SLAMS project in the USA[3] and 92 stations are operating in a 150 × 200 km area of the Netherlands.[4]

How a local value could be used to describe the situation over a large area is still a matter of discussion. This question is, however, entirely invalid in a mountainous country, where every valley and basin has its own meterological conditions and, together with local sources, its special pollution problem.

Manual and therefore inexpensive methods such as the classic Saltzman method[5] imply the problem of punctual measurements during a limited period of time. The air is purged through a solution where the nitrogen oxides are converted into nitrite ion; this gives a specific reaction with diazoting-coupling reagents to form a deeply coloured dye, which is measured photometrically.

Continuous photometric analyzers based on this procedure are rather complicated and require excessive operator attention. The efficiency of the reaction yield of the dye is still under discussion.[2,6,7]

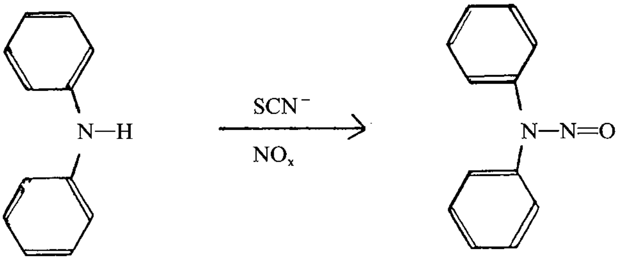
The summation method we describe in the following section should not be seen as a replacement for the other two as its analytical content is different.

In order to elucidate spatial variations of NO_x concentrations with a very dense network as required for deforestation studies, one must have an inexpensive method requiring minimal personal effort.

METHOD

Nitrosation of secondary amines yields nitrosamines; most of these N-nitrosamines have been shown to exhibit carcinogenic activity. This fact has led to intensive development of analytical methods for this group of compounds down to the ppb level. When the analyst is concerned with trace amounts in various materials, such as foodstuffs, the problem of contamination is still present when nitrosamines are produced from the secondary amines in the material and from the nitrous gases present in the air.[8,9] We used this problem to develop a method for measuring nitrogen oxides in the atmosphere by exposing a secondary amine in the ambient air and taking the yield of nitrosamines as a measure of the concentration of nitrogen oxides. To avoid health risks we have chosen diphenylamine as the reagent because there is no doubt that diphenylnitrosamine displays absolutely no cancerogenic activity.[10]

For nitrosation to occur *in vitro* as well as *in vivo*, nitrite ion is not the proper agent; it has to be converted to nitrous anhydride (N_2O_3), to a nitrosyl halide (X—NO) or -pseudohalide. Among the pseudohalides, thiocyanate has the most pronounced catalytic activity.[11] In preliminary studies we exposed, in gas chambers, chromatographic paper soaked with a solution of diphenylamine in glycerol to NO_2, but no reaction occurred, whereas when we added SCN^- to the solution, rapid nitrosation could be observed. From this, we derived the following scheme for the overall reactions:



As we have not studied the reaction in detail, we cannot determine whether nitrosyl-thiocyanate is directly produced by nitrogen oxide from the air or through nitrite ion, formed by dissolving nitrogen oxide in glycerol. From an analytical standpoint this problem is less important, but the reaction considered here is fast enough to be used for this type of heterogenous reaction.

The next problem to be solved was how to keep a chemical reaction in the atmosphere going for at least a month without the attention of operators. In the case of the lead candle for SO_2 the lead oxide is suspended in a polysaccharide, the tragacanth, which retains enough humidity to support the reaction to sulphate. As in the case of nitrosation reactions of the organic type, we have to support the measuring device, the chromatographic paper impregnated with the diphenylamine, with the media over the full period of exposure time. For our outdoor measurements we fit a sheet of paper (10 × 8 cm) over the surface of a cylindric vessel made of clay (3 cm diameter, 10 cm high) glazed on all parts which are not covered by the paper. The vessel is filled with a solution of KSCN in glycerol and is sealed with a stopper. The porosity of the vessel is such that glycerol diffuses through it in sufficient quantities to support the reaction on the paper, but slowly enough to retain sufficient liquid up to about a period of six weeks. To avoid contamination by birds and to protect it against metereological influences, the candle is installed under a bell-shaped windshield (25 cm diameter, 25 cm high) with 5 holes (6 cm diameter) in it, the same as used for the lead candle.

As we will see in the next section of this paper, the dimensions of the candle are such that all different levels of nitrogen oxide pollution are attented by it, from "clean air" districts up to strongly polluted industrial areas. The evaluation of the candles is facilitated by the large number of well-developed analytical methods of nitrosamines,[12] most of which are very sensitive. Depending only on the environmental purpose the candle is exposed for a period of time ranging between a week and four weeks.

PARAMETRIZATION OF THE METHOD

To prove the reliability and effectiveness of our method, we hung out the candles in the vicinity of automatic monitoring stations working on the chemiluminescence basis. These stations cover the whole range of possible levels in nitrogen oxide pollution from a clean air forest district (no. 1 on table I), a parking area in a city (no. 12) up to a station on the top of a hill (no. 14) affected by the exhaust of a chemical plant; the distance from north to south of this controlled area is about 400 km, varying from 200 m up to 1600 m above sea level. At the same time four candles were exposed near one station to get an impression of how large the variances, expressed as the standard deviation in table I, is in the uptake of the nitrogen oxides. Discussion about variance within one set of candles is difficult to carry out because the possibility for the air flow to reach the candles in the same way was quite different, especially in cities. As we will see later, the air flow under the windshield is reduced to some kind of turbulent diffusion so that in most cases the wind speed contributes only marginally to the outcome of the method. The second apparent difference in this collocation of candles was the different height of air uptake. To reach the candles more easily, we arranged them about 2 m above ground whereas the gas inlet of the chemiluminescence station was about 4 m. The main problem for comparison is that the outcome of both methods belong to different dimensions of the same entity. Whereas the chemiluminescence measures a concentration per volume unit, summation methods measure a deposition rate of gaseous molecules on the candle surface taken as an average during a certain time. Nevertheless by the definition of the "deposition velocity",[13] both measures are linked together:

TABLE I

Daily mean yield of nitrosamine of the four collocated candles compared with the values from chemiluminescence

Station	Exposure time (days)	100% NO_2 +90% NO (mg/m^3)	Daily yield of nitrosamine (mg)
1	22	0.007	0.034±0.002
	19	0.004	0.023±0.002
2	13	0.013	0.079±0.006
	30	0.010	0.039±0.003
	26	0.009	0.047±0.012
3	14	0.013	0.078±0.008
	22	0.011	0.058±0.005
	15	0.011	0.057±0.005
4	14	0.034	0.224±0.015
	27	0.020	0.089±0.011
	14	0.045	0.200±0.011
5	13	0.047	0.185±0.017
	15	0.032	0.143±0.014
	15	0.032	0.145±0.013
	27	0.027	0.143±0.018
6	13	0.037	0.175±0.017
	14	0.045	0.248±0.010
	12	0.036	0.225±0.005
	26	0.039	0.240±0.005
7	17	0.050	0.250±0.040
	13	0.048	0.252±0.007
	13	0.030	0.284±0.033
	15	0.039	0.179±0.014
	12	0.038	0.170±0.008
	15	0.039	0.199±0.005
8	13	0.051	0.248±0.005
	14	0.062	0.309±0.008
	12	0.048	0.245±0.013
9	13	0.053	0.362±0.014
	13	0.062	0.385±0.052
	16	0.042	0.211±0.014
10	13	0.062	0.289±0.012
	14	0.067	0.332±0.015
	15	0.065	0.306±0.016
	15	0.070	0.962±0.006

TABLE I (continued)

Station	Exposure time (days)	100% NO_2 + 90% NO (mg/m^3)	Daily yield of nitrosamine (mg)
11	13	0.078	0.454 ± 0.011
	13	0.086	0.608 ± 0.027
	16	0.063	0.329 ± 0.005
	26	0.033	0.186 ± 0.011
12	17	0.099	0.652 ± 0.025
	13	0.084	0.471 ± 0.007
	13	0.086	0.547 ± 0.047
	15	0.078	0.488 ± 0.026
	12	0.055	0.276 ± 0.010
	15	0.065	0.328 ± 0.007
13	17	0.102	0.779 ± 0.006
	13	0.083	0.479 ± 0.011
	14	0.082	0.541 ± 0.017
	15	0.062	0.318 ± 0.010
	12	0.063	0.343 ± 0.036
	15	0.059	0.288 ± 0.014
14	13	0.088	0.603 ± 0.009
	13	0.096	0.805 ± 0.009
	15	0.121	1.049 ± 0.014
	12	0.122	1.104 ± 0.056

$$Vg = \frac{\text{Number of particles deposited cm}^2\,\text{s}^{-1}}{\text{Number of particles cm}^3\text{ of air}}.$$

Although this definition was introduced first for dry deposits, it seems almost relevant in some sense for gaseous pollutants and is used for them in the literature.[14] At this point we want to emphasize that the aim of a summation method is not to give a measure of pollution in the dimension of a concentration but only to allow a classification of differences in the severity of pollution.

As we did not know exactly what precise reactions were taking place on the candle it was not clear how NO and NO_2 actually react with the diphenylamine-SCN^- system. We have solved this problem in an empirical way. With a standard statistical method,[15] we fitted the daily mean yield of nitrosamine with a weighted sum of

NO and NO_2 half-hour values, which were taken from the chemiluminescence output of the same period. The best fit was given for a mixture of 100% NO_2 and 90% NO.

Figure 1 presents a graphical display of both measures for all 198 candles considered in this comparison. We have ignored candles for which we lacked data for more than 40% of the monitoring time, when the stations were out of order. The concentrations of the nitrosamine are mean values of both photometric and polarographic determinations, the results are, in most cases, within the ±5% range. Analytic methods combined with an automatic sampler, would save a lot of time when analyzing a large number of candles. The concentration of diphenylamine on the candle was chosen in such a way that, in cases of the highest content of NO_x in air, 10% of it was converted into nitrosamine.

Figure 1 demonstrates clearly that this method successfully fulfills the requirements for a summation method. It allows a distinction to

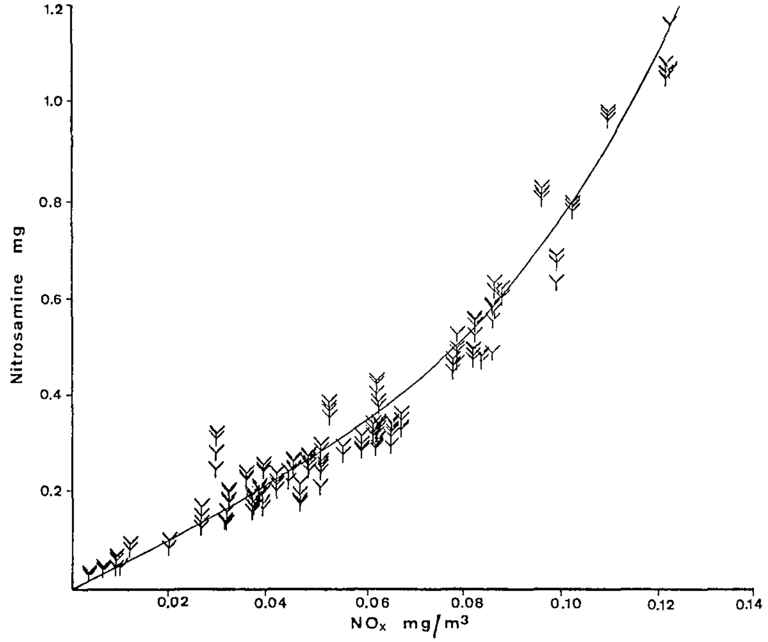


FIGURE 1 Comparison of the daily mean yield of nitrosamine per candle and the half hour mean values of the automatic stations, based on chemiluminescence.

be made between different levels of nitrogen oxide pollution much better than can be achieved for SO_2 with the lead candle. A detailed explication of the error in terms of a statistical procedure comparing the precision of the two analytical methods is restricted by the foregoing discussion. Looking at the standard deviation, given in Table I, of the four collocated candles we must bear in mind that the results were collected by outdoor measurements, which are not comparable with an experiment under controlled laboratory conditions. But although the method is primitive and the aerodynamic circumstances of every candle were different, the deviations were surprisingly small. From this the decision as to how useful the method is in an analytical sense could not be done by significant numbers but only by interpreting Figure 1.

Our calculated deposition velocities, which vary between 2×10^{-4} and $1 \times 10^{-3}\,\mathrm{cm\,s^{-1}}$, fall within the range discussed in the literature for the deposition of NO_x.[16] Together with the observed independence of the nitrosamine yield from air velocity, we can conclude that for the air stream under the windshield, there is a turbulent diffusion, an indicator for the correct construction.

Evaluation of potential interference was supported by the installation of monitors for other pollutants in the same station, such as CO, SO_2, $(CH)_n$, O_3, dry matter, beside metereological parameters like sunshine intensity, wind direction and velocity. No interference could be observed for other gases; particles with a high content of iron oxides are the only exception determined so far. Iron oxides may reduce the nitrosamine concentration, a problem which could cause errors in the vicinity of smelters.

EXPERIMENTAL

Candles

New candles[17] must be rinsed with fresh water for several hours to remove traces of nitrite present in fired clay material. A sheet of chromatographic paper of rough type, is fitted tightly over the surface of the candle by two binders. The candle is dipped into a solution of 0.22 g diphenylamine per liter ethanol. The inner part of the candle is filled with a solution of 0.23 g KSCN per liter glycerol and sealed with a stopper.

Analytical procedure

After collection, the paper must be transported in closed flask (i.e. normal test-tube) to avoid further reaction. Every sheet of paper is extracted with 50 ml ethanol.

Photometric detection

The yellow colour of the diphenylnitrosamine can be measured at 390 nm against ethanol using a 5-cm path length cell. The absorbance is stable for several hours. Beers' law is fulfilled.

Polarographic measurements

The determination of the nitrosamine by differential pulse polarography (DPP) is much more sensitive than the photometric detection, but has to be carried out very carefully. A mixture of 0.5 ml of the extract, 3 ml water, 1 ml standard phosphate buffer pH 7 and 1.5 ml ethanol is brought together in the polarographic cell. The measurements are carried out with a scan increment of 4 mV, pulse high 50 mV, the reduction peak appears at -1.12 V measured against an Ag/AgCl electrode. As several steps of reduction lay under the same peak, reversible as well as irreversible, the calibration curve is not a straight line but fits the sinh function.

CONCLUSIONS

The candle method for monitoring nitrogen oxide pollution corresponds to the needs of a summation method. The method is sensitive enough even to measure low levels of pollution and the installation of a dense net of exposed candles to resolve spatial distributions is inexpensive. In addition, evaluation is so simple that a large number of candles can be analyzed even by non-specialist personnel.

Acknowledgement

The author would like to express his appreciation to the Jubiläumsfond der Österreichischen Nationalbank, which supported this project.

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17. Candles for the purpose of proving the method will be supplied by the author free of charge.