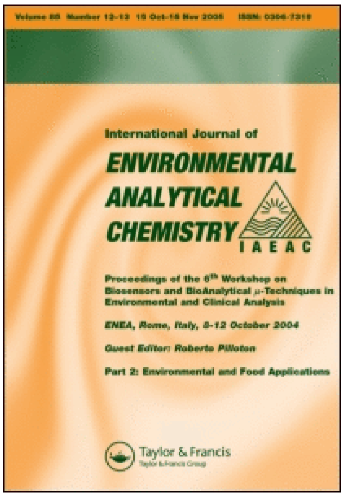

International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Indoor Nitrous Acid Levels. Production of Nitrous Acid from Open-Flame Sources

Z. Vecera[a b]; P. K. Dasgupta[a]
[a] Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX, USA [b] Institute of Analytical Chemistry, Czech National Academy of Sciences, Brno, Leninova 82, Czechoslovakia

To cite this Article Vecera, Z. and Dasgupta, P. K.(1994) 'Indoor Nitrous Acid Levels. Production of Nitrous Acid from Open-Flame Sources', International Journal of Environmental Analytical Chemistry, 56: 4, 311 — 316

To link to this Article: DOI: 10.1080/03067319408034109

URL: http://dx.doi.org/10.1080/03067319408034109

Intern. J. Environ. Anal. Chem., Vol. 56, pp. 311-316
Reprints available directly from the publisher
Photocopying permitted by license only

INDOOR NITROUS ACID LEVELS. PRODUCTION OF NITROUS ACID FROM OPEN-FLAME SOURCES

Z. VECERA[1] and P. K. DASGUPTA*

Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX 79409–1061, USA

(Received, 8 April 1993; in final form, 18 November 1993)

The concentrations of HONO in indoor atmospheres are clearly correlated with open flame sources (e.g., hydrocarbon fuel fired heaters, stoves, etc.). Relatively high levels, 20–90 ppbv, were encountered in a number of sampling sites. The half-life of HONO in a typical indoor environment appears to range from 2 to 8 h.

KEYWORDS: Nitrous acid, indoor pollution, open-flame heaters, HONO half life.

INTRODUCTION

There has been considerable interest in the indoor concentrations of oxides of nitrogen, especially NO_2. Energy efficient housing generally provides low air exchange rates and peak indoor NO_2 concentrations of 1.5 ppmv have been reported[1]. It has been recognized for some time that higher indoor concentrations of NO_x are associated with gaseous or liquid fuel fired appliances[1-8]; this source frequently dominates exposure to NO_2 rather than ambient air quality[9,10], exposure assessment models generally take this into account as well[11-13]. Adverse health effects of nitrogen oxides have been summarized[14,15]; particular concern exists about the effect of NO_2 exposure to infants and children[16,17].

The measurement of NO_2 in the above studies have largely relied on the reduction of NO_2 to NO and the measurement of the gas phase chemiluminescence of the resulting NO. Alternatively, a modified Griess-Saltzman colorimetric procedure has been used for the quantitation of NO_2 after collection by a suitable sorbent (triethanolamine, diphenylamine coated silica, sodium arsenite solution, etc.), whether by a passive sampling technique or deliberate aspiration of air. None of the above techniques differentiates NO_2 from HONO. In recent years, there has been considerable interest in the measurement of ambient

---

[1] Permanent address: Institute of Analytical Chemistry, Czech National Academy of Sciences, 611 42 Brno, Leninova 82, Czechoslovakia

HONO[18–25]. Only three studies address the specific measurement of indoor HONO[26–28]. The ratio of HONO to NO_2 from flame and post flame emissions can be as high as 0.4[28]. Because HONO readily reacts with many biogenic amines to form carcinogenic nitrosamines, this is of particular concern[29]. Specifically applicable spectroscopic techniques for HONO measurement[26] are neither affordable nor easily portable. Denuder techniques with discrete collection and measurement steps[27] provide poor time resolution. Recently we developed a reliable calibration source of gaseous HONO[18] and a portable inexpensive analyzer dedicated to the measurement of gaseous HONO and HNO_3[19]. The instrument is capable of a time resolution of ca. 20 min. We have previously reported on the ambient concentrations of nitrous acid; this varies from several hundred pptv to low single digit ppbv levels. It was of interest to examine typical indoor HONO levels and how these are affected by the operation of various appliances.

EXPERIMENTAL

The instrument has been previously described in detail[19]. Briefly, sample air is aspirated through a single tube wet effluent denuder at a rate of 1 L min^{-1}; a mass flow controller is used for flow control. Zero gas or calibration gas is sampled in an automated periodic fashion to provide quality assurance on instrument zero and span functions. The liquid effluent from the denuder is concentrated on an anion exchanger microcolumn. Periodically, the contents are eluted and the nitrate and nitrite are separated on a microseparation column. The column effluent is sent through a cadmium reductor where the nitrite passes through unaffected and nitrate is reduced to nitrite. Griess-Saltzman reagent is added to the cadmium reactor effluent, the resulting azo dye formed upon reaction with nitrite is sensed by a green light emitting diode (LED) based absorbance detector. The measurement technique is essentially free of interference from NO_2. The inlet to the wet denuder was only 10 cm long to minimize adsorption/desorption of nitric acid. Nevertheless, in all experiments, HNO_3 concentrations remained near or below the limit of detection (ca. 200 pptv HNO_3).

The experiment period ranged from late February to early March; at this location heating of living space is typically necessary at this time of the year.

RESULTS AND DISCUSSION

The first sampling location was the living room of a small family residence. The kitchen, immediately adjacent to the living room, had a volume of ca. 40 m^3 and all appliances were electrically operated. The living room, with a vaulted ceiling, encloses ca. 15 m^3. Heating in the house is provided by a natural gas furnace and forced air circulation over a sealed heat exchanger. Additionally, the living room was provided with a natural gas-fired fireplace vented through a chimney. The sampling point was located 4 m from the fire place, 2 m from the entrance to the kitchen at a height of 1.2 m from the ground. HONO concentrations ranged from 0.73 to 1.5 ppbv. We were unable to correlate the fluctuations within these

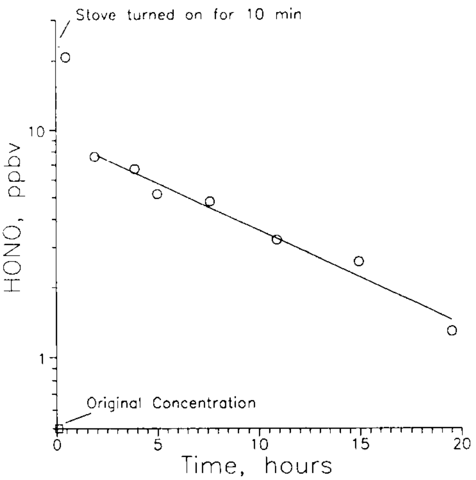

Figure 1 Formation and decay of HONO in a small air force base residential quarter upon turning on the stove for 10 min. Note logarithmic ordinate and first order decay of the generated HONO.

levels with the usual markers (e.g., whether main heating, fireplace or kitchen appliances are operating, day or night, etc.). The only observable general relationship was a decrease in the HONO concentration with the onset of ventilation.

The second sampling location was a senior officer's quarters within a regional Air Force base. The sampling point was 5 m away from the natural gas burning cooking stove in the kitchen, of a volume of ca. 30 m^3. The initial levels of HONO, with the heating system (similar to that in the previous location) on, varied between 0.5 to 1 ppbv. Then the gas stove was turned on for 10 min. The HONO level rapidly exceeded 20 ppbv and then decreased in an exponential fashion with a half life of ~ 7.5 h (Figure 1).

A more graphic example of the buildup of HONO from natural gas fired open-flame sources and its dependence on ventilation is shown in Figure 2. These results are from a small residence with an interconnected living room (ca. 40 m^3) and a bedroom (ca. 30 m^3). The sampling location was about 1.5 m from a natural gas fired heater with a ceramic radiator. The bedroom contains a separate, smaller gas-fired heater. Initially the door to the bedroom was closed and the background levels of HONO were below 1 ppbv. With the onset of the evening, the living room heater was turned on for 30 min and the HONO levels rose to ca. 70 ppbv before beginning to decrease. The decay during the first 4 h follows an exponential pattern with a half-life of ~ 2.8 h. Subsequent to this, the door to the bedroom was opened and the bedroom heater was actuated for two brief (10 min) periods That the instrument sensed the formation of HONO from this activity is clearly apparent. Following this, the outside door to the living room was opened and the HONO concentration dropped rapidly. Apparently this did not result in complete air exchange within the house—the concentration rose upon closing the door. It is also possible that HONO is reversibly desorbed from the available surface. Again the concentration decreased rapidly as the door was opened and rose again, more slowly, as the door was closed. Note that the measurements

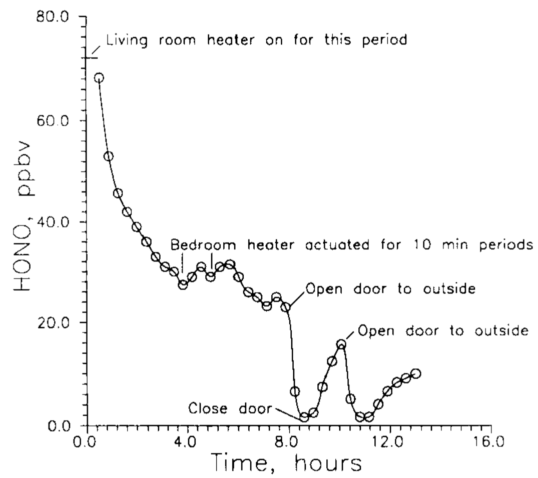

Figure 2 Formation and decay of HONO formed from gas-fired room heaters as a function of normal activities in a small residence.

were made during routine activities in this household and the levels of HONO exposure from gas-fired open-flame heaters can obviously be quite substantial. In the same household, the HONO levels in the kitchen (ca. 20 m^3) during the evening hours varied between 10 and 20 ppbv without the cooking stoves on. After two gas stoves were used for 58 min, the HONO concentration measured in the kitchen, at a distance of 3 m from the stove, rose to 90 ppbv.

The fourth measurement location was a small two-bedroom apartment with all-electric kitchen and central heating arrangements. HONO levels were below 1 ppbv and fluctuations could not be correlated to household activities. Similar results were obtained in a larger fully electric home; the HONO levels were below 0.5 ppbv. However, at this location, the HONO levels increased consistently in the early evening hours (1730–1830) to ca. 1.2–1.5 ppbv. This was most probably associated with primary emission of HONO from vehicular traffic; the house was situated ~ 30 m from a major thoroughfare.

Finally, HONO levels were measured inside a motor home of ~ 80 m^3 interior volume. NO_x levels inside mobile homes have been previously reported[30]. A kerosene-fueled space heater or a cooking stove (fueled by liquefied petroleum gas) was turned on for brief periods, following which the HONO level decayed exponentially. Regardless of the source of HONO and the initial level, it has been observed repeatedly (for the data shown in Figure 3 as well as in other experiments) that the half-life of decay at this location remains 2.2 ± 0.2 h.

The mechanisms of HONO formation remains unclear. The reaction

$$2NO_2 + H_2O = HONO + HNO_3 \qquad (1)$$

via a heterogeneous mechanism involving the action of NO_2 on a NO_2-H_2O complex adsorbed on surfaces[31] cannot be an important pathway—despite the existence of efficient sinks of HNO_3 (virtually all indoor surfaces), it is not probable that HNO_3 levels below 200

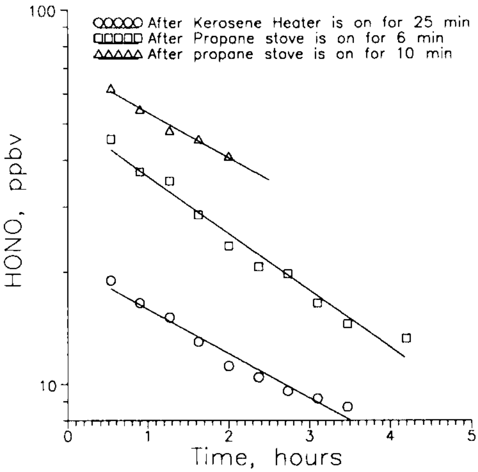

Figure 3 Formation and decay of HONO in a motorhome as a result of operating kerosene or propane burning open flame appliances for indicated periods and subsequent first order decay.

pptv with HONO levels approaching 100 ppbv can be explained if reaction *1* is a major mode of HONO production[28]. The ternary reaction

$$NO + NO_2 + H_2O = 2HONO \qquad (2)$$

is too slow to be of consequence. The clear association of HONO with open flame sources instead suggests that the reaction

$$NO + \cdot OH = HONO$$

is involved. It is well known that ·OH is produced in large concentrations in flames, especially in post flame regions[32].

To our knowledge, no clinical studies exist on the effects of HONO exposure on humans. No specific studies exist either on the measurement of nitrosamines in the proximity of significant HONO sources. Neither is it known if *in-vivo* formation of nitrosamines can occur from inhaled HONO. In view of the very substantial human exposures to HONO that occur routinely, such studies are clearly warranted.

Acknowledgement

This work was supported by the U. S. Environmental Protection Agency through R815928-01-0 and the State of Texas Advanced Research Program. However, this manuscript has not been reviewed by the U.S. Environmental Protection Agency and no endorsement should be inferred.

References

1. I. F. Goldstein, L. R. Andrews and D. Hartel, *Atmos. Environ.*, **22,** 2127–2139 (1988).
2. P. B. Ryan, M. L. Soczek, R. D. Treitman, J. D. Spengler and I. H. Billick, *Atmos. Environ.*, **22,** 2115–2125 (1988).
3. D. Noy, B. Brunekreef, J. S. M. Boleij, D. Houthuijs and R. DeKoning, *Atmos. Environ.*, **24A,** 2903–2909 (1990).
4. M. C. Marbury, D. P. Harios, J. M. Samet and J. D. Spengler, *J. Air Poll. Contr. Assoc.*, **38,** 392–398 (1988).
5. D. J. Moschandreas, S. M. Relwani and E. H. Luebocke, *J. Air Waste Management Assoc.*, **40,** 359–361 (1990).
6. E. D. Palmes, C. Tomczyk and A. W. March, *J. Air Poll. Contr. Assoc.*, **29,** 392–393 (1979).
7. R. J. W. Melia, C. du V. Florey, S. C. Darby, E. D. Palmes and B. D. Goldstein, *Atmos. Environ.*, **12,** 1379–1381 (1978).
8. E. D. Palmes, C. Tomczyk and J. DiMattio, *Atmos. Environ.*, **11,** 869–872 (1977).
9. J. J. Quakenboss, J. D. Spengler, M. S. Kanarek, R. Lentz and C. P. Duffy, *Environ. Sci. Technol.*, **20,** 775–783 (1986).
10. J. D. Spengler, C. P. Duffy, R. Lentz, T. W. Tibbits and B. G. Ferris, Jr., *Environ. Sci. Technol.*, **17,** 164–168 (1983).
11. E. Drye, H. Ozkaynak, B. Burbank, I. H. Billick, P. E. Barker, J. D. Spengler, P. B. Ryan and S. D. Colome, *J. Air Poll. Contr. Assoc.*, **39,** 1169–1177 (1989).
12. J. E. Borrazzo, J. F. Osborn, R. C. Fortmann, R. L. Keefer and C. I. Davidson, *Atmos. Environ.*, **21,** 299–311 (1987).
13. B. P. Leaderer, R. T. Zagraniski, M. Berwick and J. A. J. Stolwijk, *Atmos. Environ.*, **21,** 361–368 (1987).
14. *Air Quality Guidelines for Europe* (World Health Organization, WHO European Publication Series No. 23, WHO, Copenhagen, Denmark, 1987).
15. *Nitrogen Oxides and Their Effect on Health.* (S. D. Lee, Ed. Ann Arbor Science, Ann Arbor, MI, 1980).
16. D. P. Harlos, M. Marbury, J. Samet and J. D. Spengler, *Atmos. Environ.*, **21,** 369–76 (1987).
17. B. Brunekreef, D. Houthuis, J. Dijkstra and J. S. M. Boleij, *J. Air Waste Management Assoc.*, **40,** 1252–6 (1990).
18. Z. Vecera and P. K. Dasgupta, *Environ. Sci. Technol.*, **25,** 255–260 (1991).
19. Z. Vecera and P. K. Dasgupta, *Anal. Chem*, **63,** 2210–2216. (1991).
20. B. R. Appel, A. M. Winer, Y. Tokiwa, and H. W. Biermann, *Atmos. Environ.*, **24A,** 611-16 (1990).
21. Y. Kanda and M. Taira, *Anal. Chem.*, **62,** 2084–7 (1990).
22. M. O. Rodgers and D. D. Davis, *Environ. Sci. Technol.*, **23,** 1106–12 (1989).
23. A. Sjödin, *Environ. Sci. Technol.*, **22,** 1086–1089 (1988).
24. I. Allegrini, F. DeSantis, V. DiPalo, A. Febo, C. Perrino and M. Possanzini, *Sci. Total Environ.*, **67,** 1–16 (1987).
25. R. Atkinson and A. M. Winer, *Measurement of* NO_2, HONO, HCHO, PAH, Nitroarenes and Particulate Mutagenic Activities During the Carbonaceous Species Methods Comparison Study (Final Report, California Air Resources Board, Sacramento, CA February 1988).
26. J. N. Pitts, Jr., H. W. Biermann, E. C. Tuazon, M. Green, W. D. Long and A. M. Winer, *J. Air Poll. Control. Assoc.*, **39,** 1344–1347 (1989).
27. M. Brauer, P. Koutrakis and J. D. Spengler, *Environ. Sci. Technol.*, **23,** 1408–1412 (1989).
28. M. Brauer, P. B. Ryan, H. H. Suh, P. Koutrakis, J. D. Spengler, N. P. Leslie and I. H. Billick, *Environ. Sci. Technol.*, **24,** 1521-1527 (1990).
29. D. Grosjean, *J. Air Waste Management Assoc.*, **41,** 306–311 (1991).
30. M. Petreas, K.-S. Liu, B.-H. Chang, S. B. Hayward and K. Sexton, *J. Air. Poll. Contr. Assoc.*, **38,** 647–651 (1988).
31. M. E. Jenkin, R. A. Cox and D. J. Williams, *Atmos. Environ.*, **22,** 482–98 (1988).
32. I. Glassman, in: *Combustion* (Academic Press, NY 1987), p. 326.