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Dimethylnitrosamine Detection and Measurement using Laser Raman Spectroscopy*

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The Raman spectra of various concentrations of dimethylnitrosamine in water have been measured. The lowest concentration detected was 10 mg/l. Instrumental parameters were varied to optimize the signal response.

Index Headings. Laser Raman spectroscopy; Dimethylnitrosamine detection; Dimethylnitrosamine measurement.

INTRODUCTION

Dimethylnitrosamine (DMNA) is formed as an intermediate in the synthesis of the rocket fuel unsymmetrical dimethylhydrazine (UDMH) from dimethylamine, and is found in trace amounts in the final product. DMNA has recently received considerable public attention because of its reported cancer-inducing properties,[1] and has been placed high on the list of toxic chemicals.[2] USAF operations which involve UDMH pose a dual hazard: the toxicity of UDMH and, more importantly, the carcinogenicity of DMNA. Thus, there is a present need to monitor trace amounts of this chemical in a real environment situation where it is produced, used, and stored. Many methods of detection and measurement are available; however, laser Raman spectroscopy has been chosen for this feasibility study for several reasons: (1) DMNA is highly water-soluble, and Raman scattering from water is quite weak—thus, water should not interfere significantly; (2) DMNA has two intense Raman active vibrational modes which could be used for quantitation; and (3) high-power lasers for Raman spectroscopy are now available which should help in observing constituents at high dilution. The objective of this effort is to determine the feasibility of

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the detection and measurement of DMNA in H_2O using laser Raman scattering techniques and to optimize various instrumental parameters for low concentration measurements.

I. EXPERIMENTAL

Research grade dimethylnitrosamine was obtained commercially and used without purification. The following concentrations were made by dilution with distilled water under a N_2 atmosphere: 10 000, 1000, 500, 100, 50, and 10 mg/l.

Raman spectra were recorded on a Cary 82 Raman spectrophotometric system, using the 514.5 nm line of a Spectra-Physics model 170-03 argon ion laser as the excitation source. A 90° scattering geometry was used for all measurements, while laser power output was varied from 0.5 to 2.5 W at the sample. Samples were contained in a quartz cuvette. A multipass liquid cell was tested, but higher scattering levels encountered in this cell necessitated exclusive use of the cuvette. For each measurement, a 500 μl aliquot was used; this small amount was adequate because of the focused beam on the spot coincident with the image of the monochromator slit (approximately 5 mm in height, 0.08 mm in width). Two vibrational modes were monitored in these studies. 688 cm^{-1}, an O—N—N bend; and 1384 cm^{-1}, a methyl deformation.[3] At the lower concentrations, however, because of the increased scattering levels below 700 cm^{-1}, only the 1384 cm^{-1} band was measured. In determining the relative intensities corresponding to concentrations only peak height intensities were used. Certain precautions were exercised in recording the spectra of DMNA since sample integrity is of paramount importance for quantitative measurement. The complete spectrum from 0 to 4000 cm^{-1} at high gain was recorded to check for extraneous bands; none were found. Samples recorded under 0.5 W excitation, then recorded under 2.5 W excitation, were recorded again under 0.5 W for several days. No spectral changes were observed; therefore, it was concluded that sample integrity had been maintained. Furthermore, since there is no literature reference to decomposition under visible radiation, it was assumed initially that none would occur. The spectral results reaffirmed this assumption.

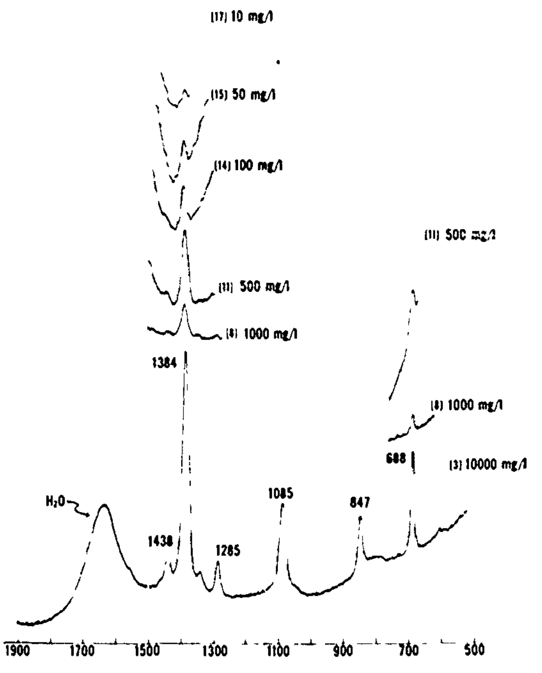

FIG. 1. Raman measurements of dimethylnitrosamine in water at various concentrations. (The numbers in parentheses, adjacent to the milligrams per liter level, correspond to the sample recording numbers as listed in Table I.)

II. RESULTS AND DISCUSSION

In Fig. 1 are shown the results for the concentration measurements of DMNA. The complete spectrum from 500 to 1900 cm^{-1} for the 10 000 mg/l sample is shown while the 688 and 1384 cm^{-1} bands are shown for the lower concentrations. The relative intensities for the prominent bands are somewhat different, compared to the spectrum reported by Levin *et al.*[3] for the liquid and solid phase Raman spectra. Especially evident is the change in Raman intensity of the 688 cm^{-1} band vs the 1384 cm^{-1} band in the liquid and water solution. In the liquid phase, the 688 cm^{-1} mode is the strongest band, with the 1384 cm^{-1} mode being only of moderate intensity. As seen in Fig. 1, however, the 1384 cm^{-1} band dominates the spectrum, with the 688 cm^{-1} band being only moderately strong. This change in intensity distribution could possibly result from the resonance structures

which have been used to explain frequency shifts observed in going from nonpolar to polar solvents. Resonance form B arises in polar solvents, as noted by Williams *et al.*[4] in their study of DMNA in carbon tetrachloride and methylene bromide in which they noted band shifts for modes whose motions involved the N—N—O moiety. A later study by Rodemacher and Lüttke[5] incorporated more solvents, but the results agreed with the work by Williams *et al.* Both resonance structures are present in water. The resulting effect is that the N—N—O group assumes a more rigid form and probably becomes slightly associated in water through dipolar coupling, while the methyl groups remain relatively free and unassociated. This structure change is believed to cause a decrease in intensity for the 688 cm^{-1} mode, with a corresponding increase for the 1384 cm^{-1} mode. The change in the position of the band at 1085 cm^{-1} is another example of the existence of resonance form B. This is a N—N stretch and appears at 1045 cm^{-1} for the pure liquid. Because of the increase in double bond character of the N—N bond, this mode has shifted to a higher frequency.

Shown also in Fig. 1 are the intensities observed for the 1384 and 688 cm^{-1} modes at the concentrations indicated. In Table I is a summary of the results obtained for the concentration and relative intensities vs selected parameters, such as spectral bandwidth (cm^{-1}), gain (counts per second), and laser power at the sample (watts). In Fig. 1 the numbers in parentheses correspond to the sample recording numbers as given in Table I. In Figs. 2 and 3 are shown plots of intensity vs concentration for the two spectral bands, 688 and 1384 cm^{-1}, at laser powers of 0.5 and 1.5 W, respectively. The graphs show very good linearity between DMNA concentration and Raman intensity. The instrumental parameters remaining unchanged were spectral band width (3 cm^{-1}) and gain (50 000 cps). Essentially, by increasing the laser power from 0.5 to 1.5 W (factor of 3), the intensity also increased by a factor of 3. This can be shown by comparing sample recording numbers (1) and (2) in Table I; by multiplying the intensities 4.6 and 11.5 by 3, giving 13.8 and 34.5, respectively, these results compare favorably with the intensities actually observed in sample recording number (1) (13.8 and 34.4, respectively). There is good agreement of theory and experiment between the changes in concentration and the corresponding relative intensities; for example, the results for the 10 000 mg/l sample show relative intensities for the 1384 and 688 cm^{-1} bands as 11.5 and 4.6, and for the 1000 mg/l sample, the intensities are 1.2 and 0.5. This corresponds to a 10-fold decrease in concentration which from the spectral measurements is approximately correct. Other similarities exist between the other parameters and concentration and the observed relative and predicted intensities. The lowest detectable concentration was the 10 mg/l sample. As mentioned earlier, only the 1384 cm^{-1} mode was used for concentration and intensity correlation because of the high scattering below 800 cm^{-1} at milligrams per liter levels less than 500. At high gain levels, high laser power, and wide slits, the noise and scatter increased dramatically. For this case, best optimum conditions were: spectral bandwidth of 6 cm^{-1}; gain of 5000 cps; and laser power of 2.5 W at the sample. Even under 2.5 W excitation, sample integrity remained unchanged after several days of experimentation. For the small value milligrams per liter samples, in particular, the high laser power output was a definite asset.

TABLE I. Concentration and relative Raman intensity measurements for dimethylnitrosamine in water.

Sample recording no.[a]	DMNA conc (mg/l)	Spectral bandwidth (cm^{-1})	Gain (cps × 1000)	Laser power at sample (W)	Raman intensity (arbitrary units)	
					688 cm^{-1}	1384 cm^{-1}
(1)	10 000	3	50	1.5	13.8	34.4
(2)	10 000	3	50	0.5	4.6	11.5
(3)	10 000	3	10	0.5	29.5	70.7
(4)	10 000	3	5	0.5	50.5	100.+
(5)	1000	3	50	1.5	1.1	2.7
(6)	1000	3	50	0.5	0.4	1.0
(7)	1000	3	10	0.5	1.5	4.8
(8)	1000	3	5	0.5	4.9	10.0
(9)	500	3	50	1.5	0.6	1.6
(10)	500	6	50	1.5	2.9	6.7
(11)	500	12	50	1.5	9.0	22.2
(12)	500	3	50	0.5	0.2	0.6
(13)	100	6	50	1.5	···	1.2
(14)	100	6	5	1.5	···	11.5
(15)	50	6	5	2.5	···	9.1
(16)	50	6	5	1.5	···	7.3
(17)	10	6	5	2.5	···	2.6

[a] Numbers are also keyed to data in Fig. 1.

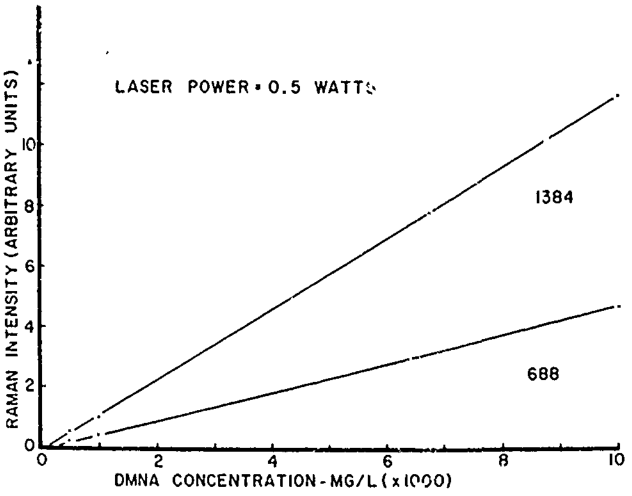

FIG. 2. Graph of Raman intensity vs DMNA concentration for the 1384 and 688 cm^{-1} bands with 0.5 W of 514.5 nm laser excitation. Instrumental parameters. spectral bandwidth = 3 cm^{-1}, gain = 50,000 cps, p = 1 s, scan speed = 1 cm^{-1}/s.

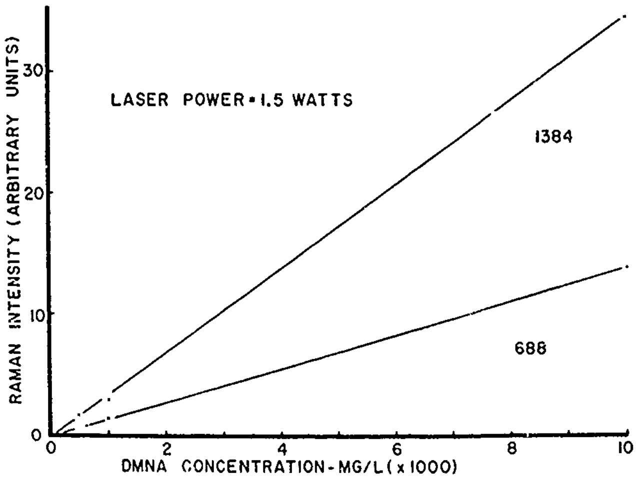

FIG. 3 Graph of Raman intensity vs DMNA concentration for the 1384 and 688 cm^{-1} bands with 1.5 W of 514.5 nm laser excitation. Instrumental parameters· spectral bandwidth = 3 cm^{-1}, gain = 50,000 cps, p = 1 s, scan speed = 1 cm^{-1}/s.

The principal source of error involved in these concentration intensity measurements is the variation of laser power output; this output would vary by ±5 mW from one sample to another. The variation introduces an approximate error of ±0.1 in intensity, which corresponds to an error in concentration of about ±3%. Other potential sources of error, namely, instrumental settings, solution preparation, and actual measurement of peak intensities, are considered to be negligible in comparison to the principal source of error. This conclusion is based primarily upon the reproducibility of data from several recordings using identical experimental parameters.

The main factors affecting and limiting the selectivity and sensitivity of this technique are the interferences from water- and methyl-containing compounds. For the normal Raman scattering technique the high level of scattering from water poses the real detection limit since both reference bands for DMNA fall close to water bands. When the sensitivity of the instrument is increased for low DMNA concentration levels, the water background increases also and will eventually obscure any DMNA bands. The highest sensitivity settings for the instrument are: laser power ≈ 4 W, spectral bandwidth = 20 cm^{-1}, and gain = 100 cps. By a consideration of only the instrumental limits, a theoretical detection level of 0.01 mg/l is possible. From Fig. 3 a similar theoretical value can be obtained by extrapolating the line for the 1384 cm^{-1} band to near zero intensity. The approximate corresponding concentration value is 50 mg/l; this value under the optimum experimental conditions stated previously would reduce to 1 mg/l, which is more realistic but still a factor of 10 too low for the actual observed measurement of 10 mg/l. Interferences from other compounds could pose a problem only if the compounds are similar in structure. For this study a methyl deformation and a N—N—O bend were used for identification. The N—N—O bend should be free from interference except from other dialkyl nitrosamines. For the methyl deformation, interference could come from methyl amines, methyl hydrazines, or other methyl nitrosamines; however, these other interferents each possess a unique vibration which should serve to identify it from DMNA.

In conclusion, we have demonstrated that a minimum detectable concentration of 10 mg/l of dimethylnitrosamine dissolved in H_2O can be measured by using conventional laser Raman scattering techniques. An argon ion laser operating at 514.5 nm and at least 2.5 W is desirable, as well as a low scattering sample container. Only a 500 μl sample was needed for these measurements, and it was completely stable under high power laser excitation. It should be pointed out that this was a feasibility study for an unmodified instrument and for techniques which could easily be adapted for routine analytical application. For this reason, no special techniques were applied to improve sensitivity. The technique is readily adapted for analytical application, and Raman spectroscopy offers the advantages of little spectral interference from water; however, it did not incorporate some of the "real" factors associated with sampling from the field. Compounds with similar structures will have to be regarded as potential interferents as well as fluorescent compounds remaining in solution after careful sample preparation. Thus, certain to be a main factor in the usefulness of this technique is whether interfering substances dissolved in water will obscure or obviate the bands used for identification and quantitation.

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