

TECHNICAL NOTE

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Analysis of Alkyl Nitrites by Gas Chromatography-Infrared Spectroscopy

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ABSTRACT: Gas chromatography-Fourier transform infrared spectroscopy (GC/IR) was used to analyze a series of alkyl nitrites (butyl and pentyl) as well as some typical "street products" containing alkyl nitrites. The vapor phase IR spectra of the nitrites exhibited strong absorbances near 1665 and 1620 cm^{-1} (anti and syn R-O-N=O stretches) and 780 cm^{-1} (O-N stretch); yet enough variation exists to distinguish between them. Street samples, or purposely "aged" nitrites, showed mixtures of readily separated components consisting of alkyl nitrites and nitrous oxide.

KEYWORDS: toxicology, gas chromatography, infrared spectroscopy

Alkyl nitrites can be purchased as room odorizers sold under trade names such as "Rush." These compounds are of forensic science interest because of their potential for abuse. The nitrites are administered by inhalation and cause a "rush" due to vasodilation of the blood vessels in the brain. Toxic effects of nitrite abuse include nausea, dizziness, headache, sedation, hypotension and tachycardia. Direct ingestion of the liquid nitrites has proven to be fatal [1]. Many states have legislation controlling their use as intoxicating compounds.

The identification of alkyl nitrites by use of gas chromatography-mass spectroscopy has been reported [2]. The extensive use of common lower molecular weight ion fragments in the identification process poses some problems in differentiation among alkyl nitrites. For example, a listing of the eight most abundant fragment ions from the mass spectrum of a series of alkyl nitrites revealed that all contained the same 6 fragment ions at m/e 27, 29, 30, 41, 43 and 57 [2]. Gas Phase Infrared Spectroscopy has also been used to successfully identify amyl and butyl nitrites [3]. However, the spectra obtained were most probably composite spectra consisting of the nitrite and any other volatile substance that might have been present. In an attempt to improve on these methods, a study was undertaken to explore the feasibility of identification of nitrites by GC/IR.

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Experimental Procedure

Preparation of Alkyl Nitrites

An adaptation of a literature method [2] was used. A mixture of 0.2 mL water, 0.25 mL concentrated sulfuric acid, and 1 mL of the appropriate alcohol was placed in a 50 mL test tube, sealed and chilled in an ice bath. A solution (1.38 M) of sodium nitrite (2.8 ml) was added dropwise over the period of 10 min with periodic shaking. The solution was shaken at five minute intervals for another hour, then allowed to stand for 10 min to permit the separation of the alkyl nitrite from the aqueous layer. The upper alkyl nitrite layer was transferred to a small vial and sealed.

Instrumentation

Analyses were performed using a Hewlett-Packard 5890 gas chromatograph attached to a Nicolet 5SXC IR with an MCT detector. The column used was a Hewlett-Packard HP-5 crosslinked 5% phenyl/methyl silicone capillary column, 25 m by 0.32 mm id, with 1.05 μm film thickness. The gas chromatograph was operated in the splitless mode with the injector at 100°C and the oven held at 40°C. The transfer line from the GC column to the IR was set at 150°C with the light pipe set at 155°C. Injections consisted of 0.5 cc of the headspace gasses from the product or sample vials. The spectra were determined from 4000 to 600 cm^{-1} .

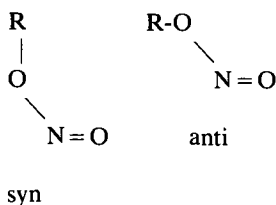
Results

IR spectra were obtained for butyl nitrites (Fig. 1), pentyl nitrites (Fig. 2), and isopropyl nitrite (Fig. 3). An aged sample of n-pentyl nitrite was analyzed in order to identify the products resulting from the decomposition of alkyl nitrites (Fig. 4). Four commercially available nitrites [4], Black Jac, Gaz, Head, and Texas Gold were analyzed (Fig. 5) and their contents identified (Fig. 6 and 7).

Discussion

The IR spectra for the nitrites exhibited strong absorbances at 2880-3000 cm^{-1} (due to the C-H stretching) at 1665 and 1620 cm^{-1} (due to anti and syn N=O stretching modes), and at 780 cm^{-1} due to the O-N stretch. The results are summarized in Table 1 for the authentic nitrite samples tested. These peaks, in conjunction with the fingerprint region, 1500 to 600 cm^{-1} , offered sufficient variations to differentiate between the compounds.

Tertiary nitrites are easily identified by a single peak attributed to the anti form in the N=O stretching region and two peaks in the O-N stretching region. The bulkier secondary and sec-butyl nitrites exhibited only weak syn N=O stretching peaks at 1620 cm^{-1} in comparison to the more intense anti peaks at 1665 cm^{-1} . With the less hindered primary alkyl nitrites, the syn N=O stretch grew somewhat stronger at the expense of the anti signal. Isopropyl nitrite gave a unique spectrum containing a shoulder above 1700 cm^{-1} on the shorter wavelength end of the twin N=O stretches.



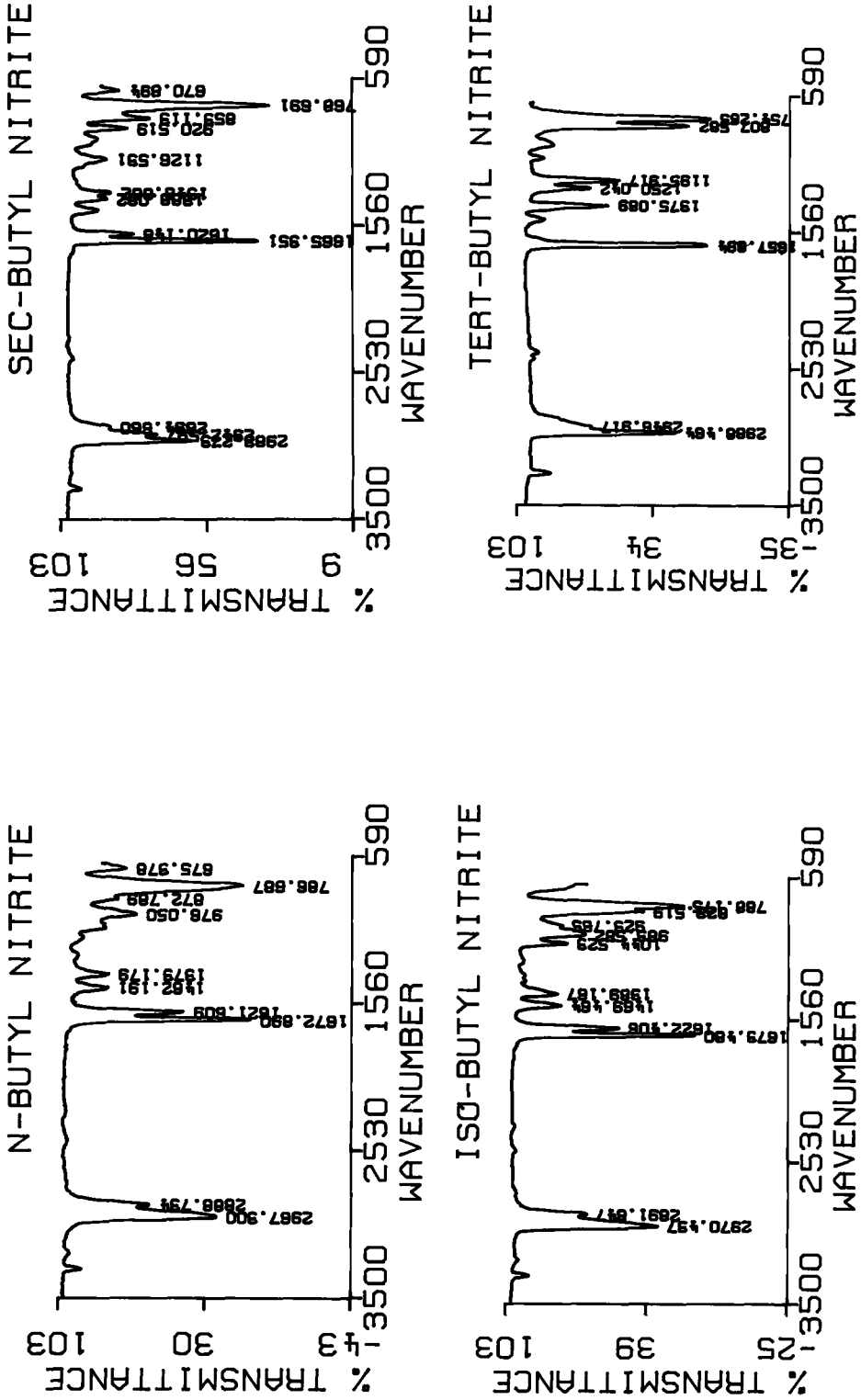


FIG. 1—IR spectra of butyl nitrites.

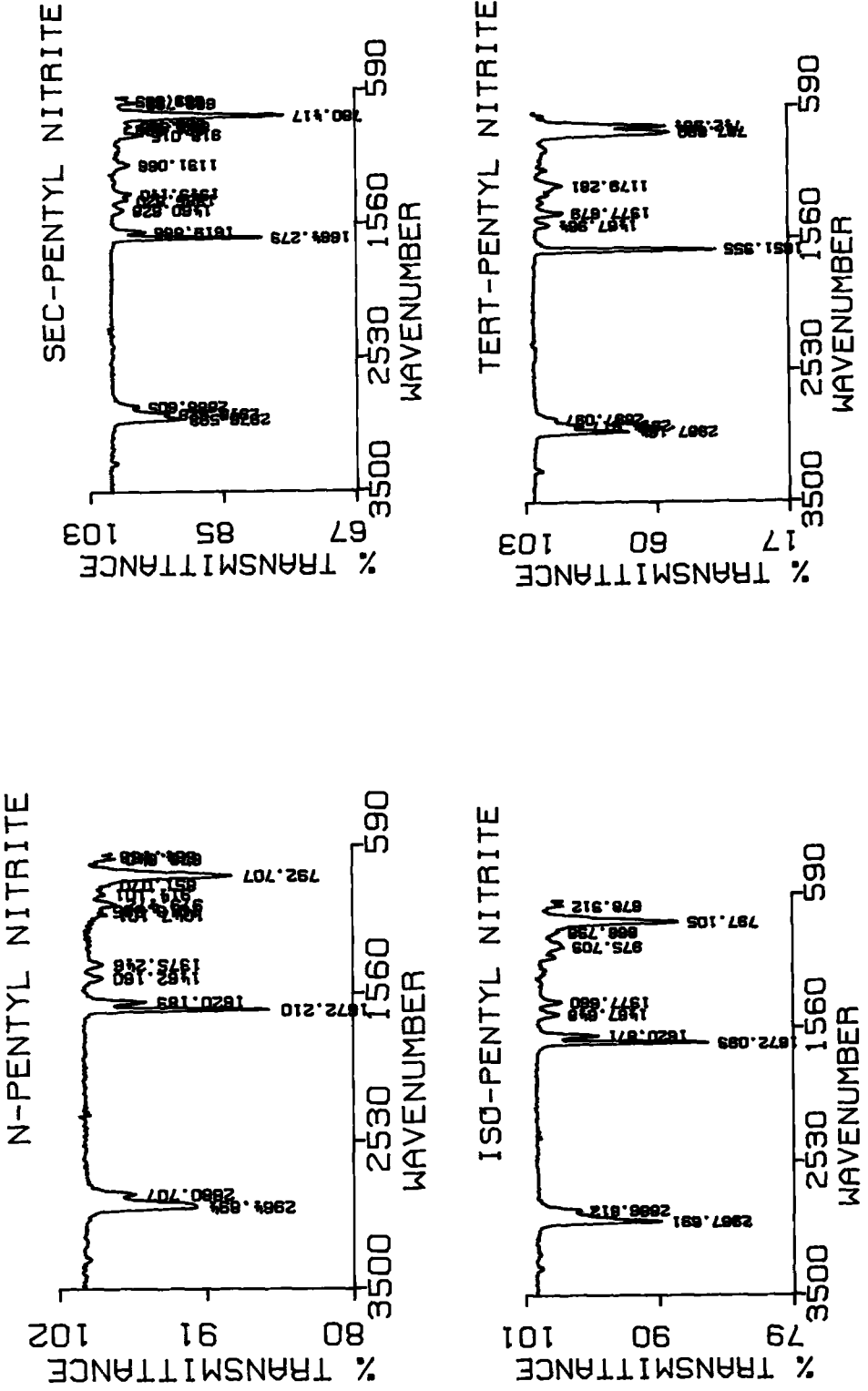


FIG. 2.—IR spectra of pentyl nitrites.

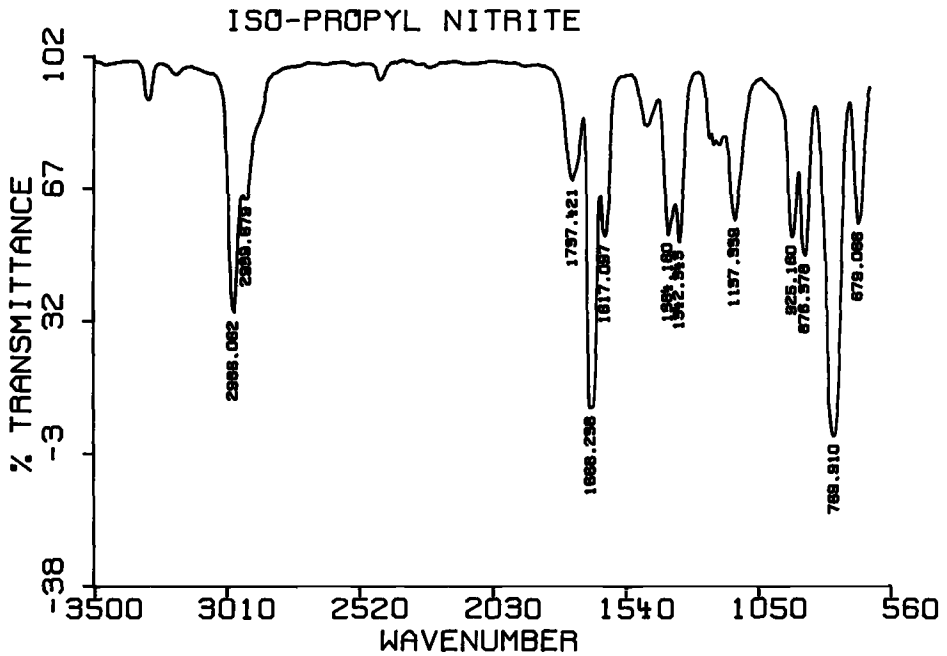


FIG. 3—IR spectrum of isopropyl nitrite.

The presence of three peaks in the C-H stretching region was unique and therefore useful in identifying the sec-alkyl nitrites. Although the spectra for the primary alkyl nitrites (*n*- and iso-) were fairly similar to each other, the isoalkyl nitrites had a more intense peak for the C-H stretch at 2968 cm^{-1} in comparison to the peak at 2890 cm^{-1} . Isoalkyl nitrites also exhibited a peak near 980 cm^{-1} that was broader than the corresponding peak for the *n*-alkyl nitrites. In general, pentyl nitrites were weaker absorbers than their butyl counterparts.

When an aged sample of *n*-pentyl nitrite was analyzed, three readily identifiable peaks were observed (Fig. 4). Nitrous oxide (peak #1) was the major component. In addition to a significant amount of *n*-pentyl nitrite (peak #3), iso-pentyl nitrite was also found to be present.

Analysis of the four commercial samples (Fig. 5) showed several different formulations. All four displayed various levels of nitrous oxide, which may have been a function of how fresh each sample was. The only nitrite component in Gaz was isopropyl nitrite. Black Jac (Fig. 6) and Head showed similar formulations consisting of primarily isopropyl nitrite with some isopentyl nitrite also present. The label on Texas Gold listed pentyl nitrite and 3-methyl-1-nitro-butane, but our analysis (Fig. 7) showed the formulation to consist of isopropyl and isobutyl nitrites.

This points to advantages of using GC/IR for alkyl nitrite analysis. Commercial samples and a purposely aged alkyl nitrite were shown to contain more than one component including significant nitric oxide. Spectra by IR alone would be composites of all the substances present. Since the typical street sample could be subject to partial decomposition due to heat, light, or exposure to the atmosphere, their analysis would often be complicated by the presence of decomposition products. Analysis by GC/IR allows prior

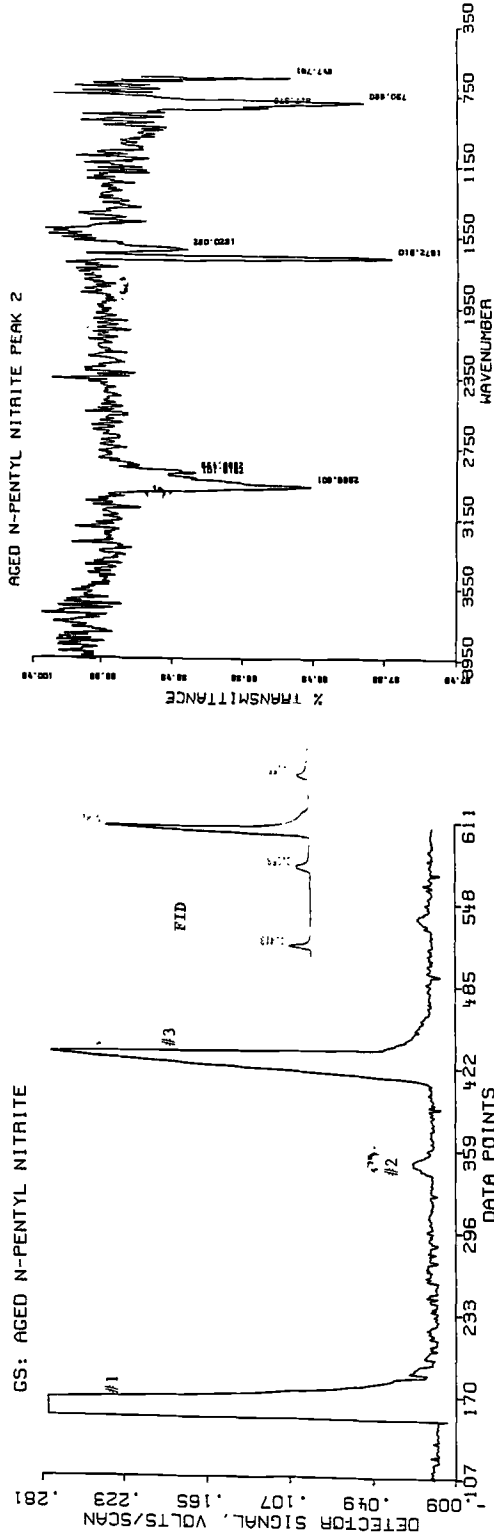


FIG. 4—GC/IR analysis of aged n-pentyl nitrite.

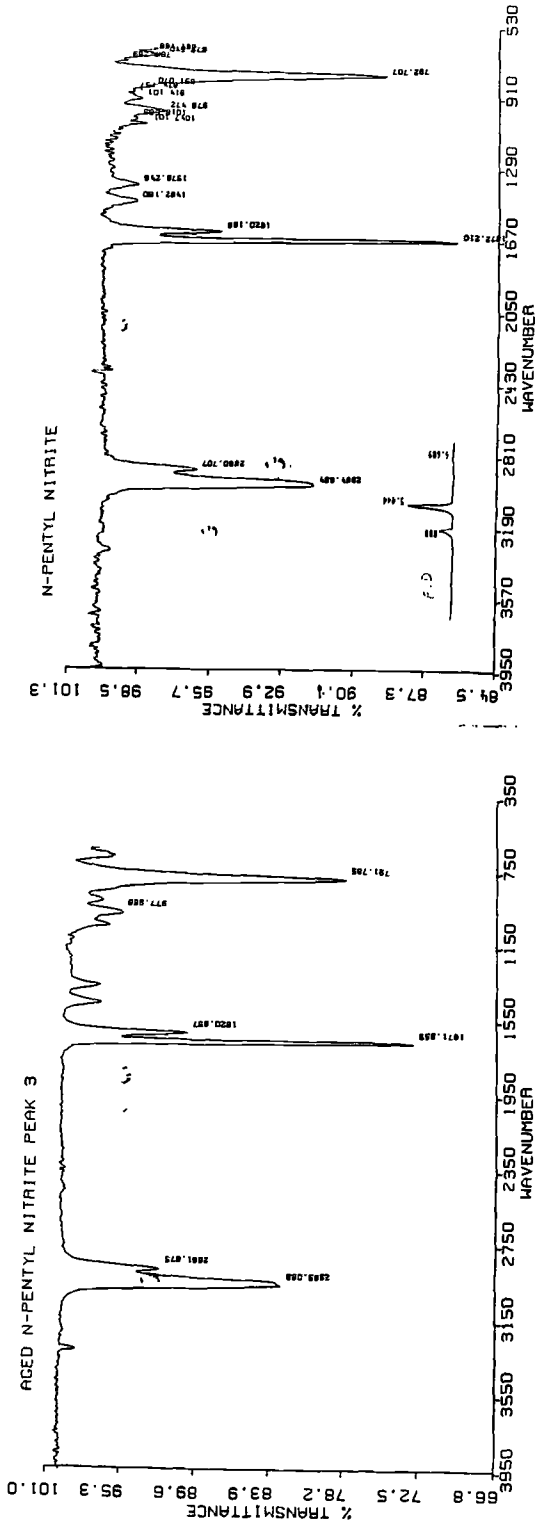


FIG. 4—Continued.

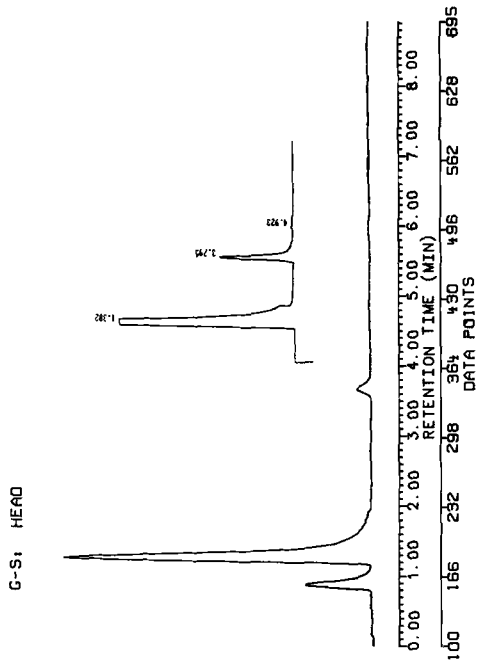
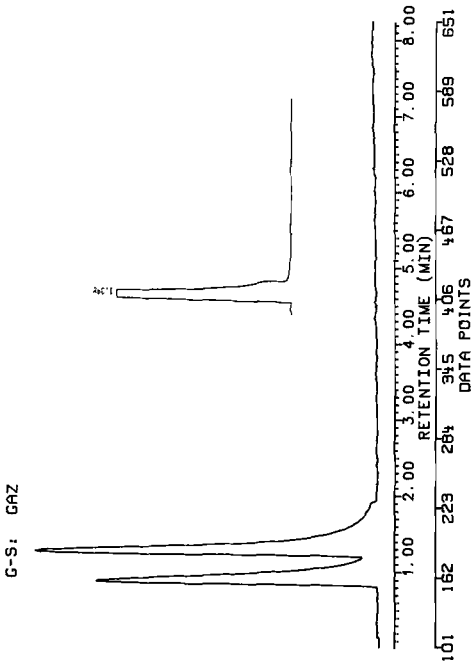
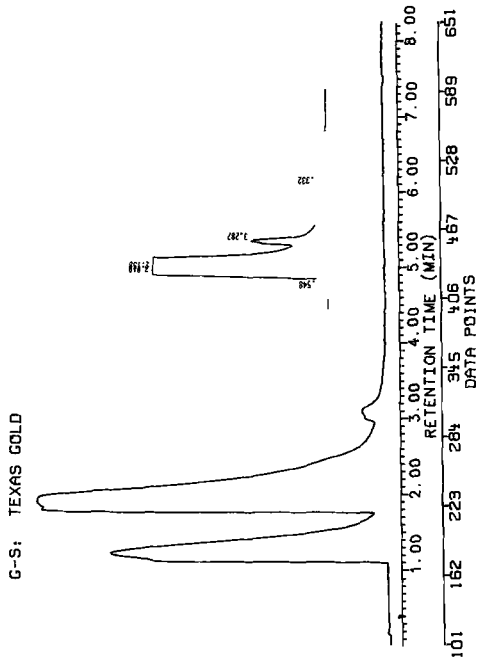
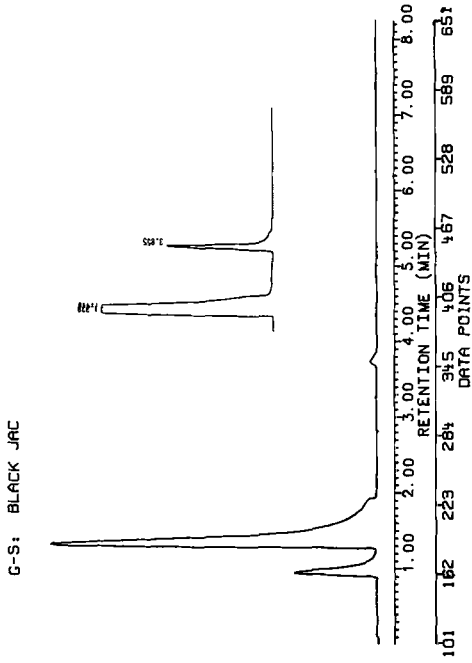


FIG. 5—Gas chromatograms of commercial alkyl nitrite products.

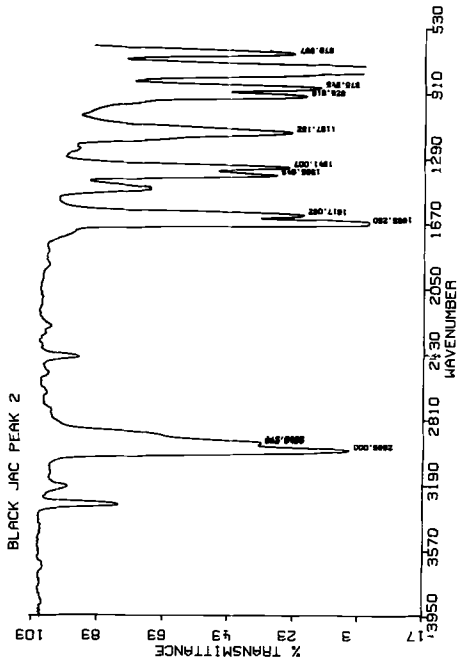
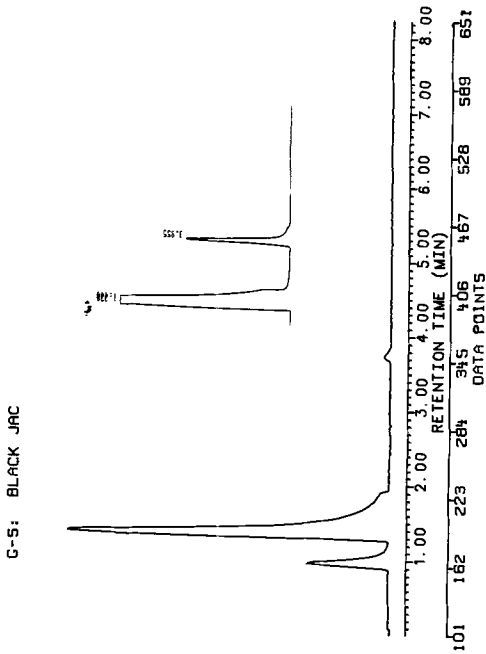
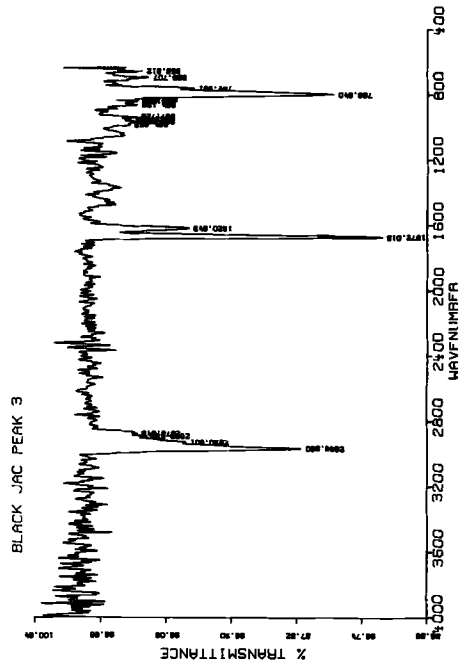
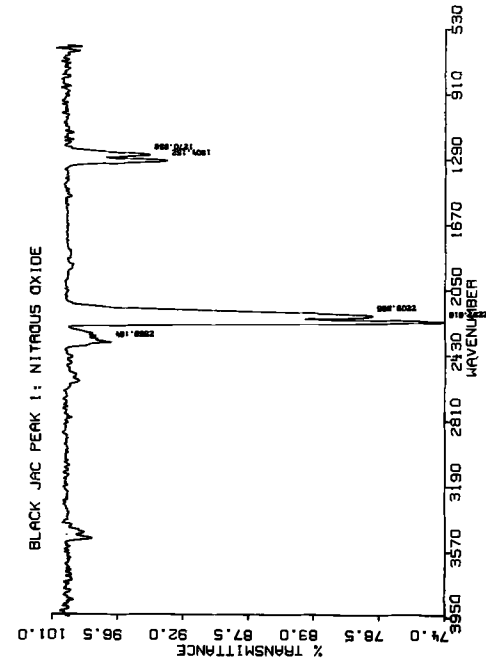


FIG. 6—GC/IR analysis of "Black-Jac."

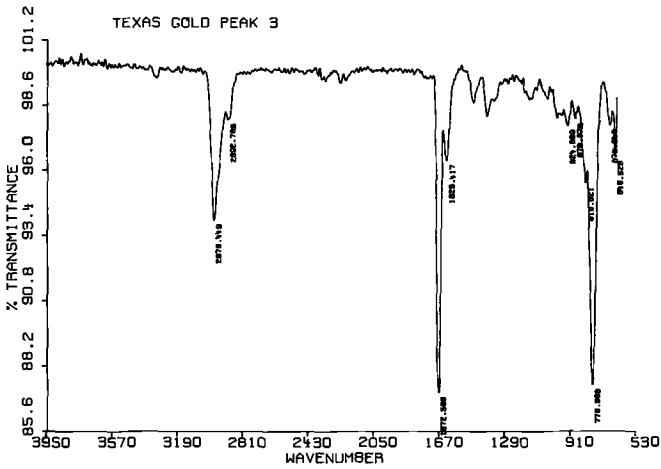
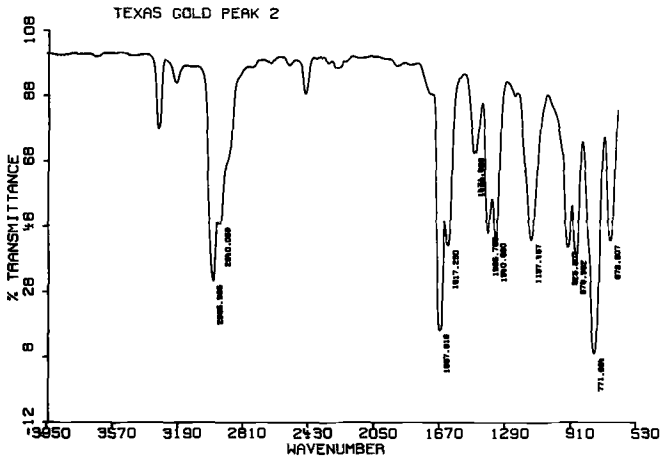
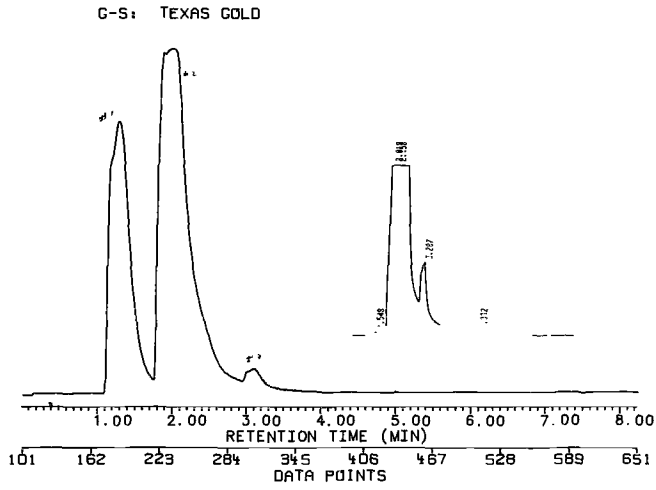


FIG. 7—GC/IR analysis of "Texas Gold."

TABLE 1—Characteristic IR peaks for alkyl nitrites.

R-ONO R =	C-H cm ⁻¹		R-O-N = O cm ⁻¹		O-N cm ⁻¹	Rel. ret. time
			anti-	syn-		
n-Butyl	2967	2889	1673	1621	787	1.0
s-Butyl	2983	2943 2895	1665	1620	853 768	0.8
t-Butyl	2989	2947	1665	1620	808 754	0.6
i-Butyl	2970	2892		1658	792	0.8
n-Pentyl	2965	2881	1672	1620	793	2.0
s-Pentyl	2977	2941 2889	1664	1620	780	1.4
t-Pentyl	2987	2945 2897		1651	788 743	1.4
i-Pentyl	2968	2887	1672	1621	797	1.6
i-Propyl	2986	2940	1668	1617	770	0.5

separation of components and gives spectra and retention times of pure compounds for identification purposes.

Conclusion

Alkyl nitrites are a volatile and somewhat unstable group of compounds that lend themselves readily to GC/IR analysis. Use of this technique allows unequivocal and rapid identification of alkyl nitrites.

References

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