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RAMAN/FTIR SPECTROSCOPY OF
OIL-SHALE-RETORT GASES

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Abstract

A Raman facility was assembled in order to aid in the evaluation of the feasibility of using Raman or FTIR spectroscopy for analyzing gas mixtures of interest in oil shale. Applications considered in oil shale research included both retort monitoring and laboratory kinetic studies. Both techniques gave limits of detection between 10 and 1000 ppm for ten representative pertinent gases. Both techniques are inferior as a general analytical technique for oil shale gas analysis in comparison with mass spectroscopy, which had detection limits between 1 and 50 ppm for the same gases. The conclusion of the feasibility study was to recommend that mass spectroscopic techniques be used for analyzing gases of interest to oil shale.

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Introduction

A feasibility study of doing oil shale gas analysis by Raman or FTIR (Fourier Transform Infrared) spectroscopy was initiated with two needs in mind. The first need was to develop an alternate technique for on-line real time retort monitoring. The current analytical technique, gas chromatography, is not only slow but occasionally suffers from sampling problems; an in-situ analytical technique would be ideal. The second need was to provide sensitive (ppm range) species-selective analysis of complex oil shale gas mixtures in the laboratory for both kinetic studies and to monitor oil characteristics (e.g., alkene/alkane ratios) as a function of processing parameters. Species of particular interest include both light hydrocarbons as well as trace pollutants (e.g., OCS, SO₂, NO_x, NH₃).

Four instrumental approaches were considered: 1) Raman spectroscopy, 2) FTIR, 3) conventional mass spectroscopy, and 4) triple quadrupole ms/ms. Raman spectroscopy offered the only possibility for true in-situ monitoring of oil shale retorts (as opposed to laboratory experiments). Although Raman instrumentation is much less commercially developed than that for the other approaches, a reasonably sophisticated facility was established in short order from various components most of which were already present on site. The other three approaches involve commercially available equipment (although the triple quadrupole ms/ms was a home-build version); the necessary instrumentation for all approaches was available on site.

Raman applications to gas analysis are less extensive than FTIR applications. Raman techniques for gas analysis can be divided into two

classifications: linear and non-linear (in laser power). All non-linear techniques^{1,2} (CARS, PARS, SRS, RIKES, inverse Raman, etc.) can be eliminated from consideration for the following reasons: 1) all non-linear cw techniques lack sensitivity³ (e.g., the limit of detection, or LOD, is approximately 10Δ); 2) all pulsed non-linear techniques are less sensitive than cw linear techniques in the environment important for oil shale gas analysis (atmospheric pressure and no luminescent background) by at least two orders of magnitude;⁴ 3) high peak power pulsed non-linear techniques are inherently difficult to quantify due to the pulse-to-pulse variability, and the required laser equipment is not readily available; 4) although the equipment was available, in principal, for high repetition rate pulsed non-linear techniques, such an approach would be hopelessly complicated for routine analysis.⁵ Consequently, only linear cw Raman techniques were considered in this feasibility study.

Raman techniques have been applied to gas analysis of hydrocarbon mixtures,⁶ environmental pollutants (e.g., SO_2 , CO_2 , NH_3 , C_2H_2 , C_2H_6 , NO , CO),^{7,8} isotopic determinations (N_2 , O_2),⁹ combustion analysis,¹⁰ and coal gasification product streams.¹¹ Although there are few references to kinetic applications of Raman spectroscopy, the expected sensitivities were on the order of 10 ppm; if these or similar sensitivities could be obtained in reasonable times (≤ 5 s) useful kinetic information could be obtained. Finally, the advent of OMA technology (optical multichannel analyzer) offered the possibility of obtaining kinetic information on several species simultaneously.

Applications of FTIR spectroscopy to gas analysis are numerous. Of particular interest are applications to tobacco pyrolysis^{12,13} and kinetics,¹⁴ polymer pyrolysis,¹⁵ transient measurements,^{16,17} kerogen carbonyl analysis,¹⁸ oil shale analysis,¹⁹ coal analysis²⁰⁻²² and pyrolysis,²³⁻²⁶ and sensitive detection of atmospheric pollutants (e.g., H_2S , C_2H_4 , CO , NH_3 , SO_2 , NO).²⁷

The mass spectroscopy approaches were pursued independently and will not be described in this paper to any great extent. However, it soon became apparent that even conventional mass spectroscopy offered substantial advantages over either Raman or FTIR spectroscopy for oil shale gas analysis.

Experimental

Figure 1, is a schematic of the Raman system assembled for this feasibility study. The core of the system was already available (i.e., a laser, monochromator, and photon counting apparatus); therefore, only the imaging peripherals were purchased for this work. A Spectra-Physics 171-09 (18 watts all lines) was the illumination source; the 514.5 nm line was used at approximately 8 W to stimulate Raman scattering.

Commercially available imaging and sampling peripherals were obtained from Spex: 1) a premonochromator (laser mate, Model 1460) to isolate the laser line and eliminate plasma irradiation; 2) the illuminator and sample chamber (Model 1459) to image the excitation source onto the sample and collect the scattered light and focus into the monochromator; 3) an external resonating cavity (Model 1443V), optimized in the visible, which was used to

obtain multiple passes through the sample cell (usually ~ 10 passes); 4) a gas cell (~ 10 cc dead volume with ~ 4 cm pathlength) with Brewster windows (Model 1443). A notch filter was used to eliminate most of the elastically scattered light (i.e., 514.5 nm) prior to the monochromator's entrance slit.

A Spex Model 1702 0.75 m monochromator with the compudrive option was used with a holographic grating, optimized for the visible and with the equivalent of 2400 g/mm. This corresponds to a bandpass of ~ 0.55 nm/mm (FWHM); routinely Raman spectra were taken with 1 cm^{-1} resolution ($50\text{ }\mu$ slit width). A single rather than a double monochromator was used because with the oil shales gases of interest, there is less scatter, no fluorescence background, more throughput, and it was available.

The Spex floating lens assembly (Model 1630c) was used to image the monochromator output onto the photomultiplier tube. A RCA (C31034A-02) photomultiplier tube was used, cooled to approximately -30°C with a Products for Research thermoelectric cooled housing. Photon counting equipment from Princeton Applied Research was used to process the signal: Model 1112 dual channel photon counter/processor and Model 1121A amplifier/discriminator. Typical dark counts were 10 cps. Typical time constants were 4 s (i.e., signal acquisition times per unit wavelength); a complete scan would take several hours. The photon counter output was recorded on a chart recorder and processed by an LSI-11 with teletype and floppy disks for subsequent data reduction.

The FTIR spectrometer used was a Digilab FTS-20C. Pathlengths used were 10 cm (50-100 cc) and 100 cm (2-4 L). Typical time constants were 5 s (total data acquisition plus computation) with 1 cm^{-1} resolution.

It is apparent that for simultaneous multicomponent analysis, FTIR spectroscopy is far superior to conventional Raman spectroscopy. Raman spectroscopy can, in principle, be given a simultaneous multicomponent analytical capability by replacing the photomultiplier tube with an OMA, but attempts to do that with a marginal Tracor Northern TN-1710 system were unsuccessful.

Synthetic gas mixtures were prepared on a manifold connected directly to the Raman gas cell. The most complex mixture contained ten components: H_2 , CO , CO_2 , OCS , H_2S , CH_4 , C_2H_4 , C_3H_8 , CH_3SH , and C_4H_4S (thiophene). Dilutions were made with nitrogen. Mixing was done by repeated freeze-thaw cycles. Gas collected in the Fischer assay of MFS-1 (24.8 gal/ton, RB 432) was used as a representative realistic oil shale retort gas sample.

Results and Discussion

Linear calibration curves were obtained with the Raman system (Figure 2). Extrapolation of these curves to a signal/noise ratio of ~ 2 provides an estimate of the sensitivity (LOD, or limit of detection). Table I summarizes the Raman results with both the synthetic gas mixture and Fischer assay gas, using 8 W, 4 s time constant, and 1 cm^{-1} resolution.

Table II summarizes the estimated LOD's for FTIR analysis (based on the synthetic mixture), using a 50-cm pathlength, 2 s time constant, and 2 cm^{-1} resolution.

It is apparent that both techniques have their advantages and disadvantages. FTIR cannot detect H_2 at all and does very poorly with H_2S and CH_3SH . On the other hand, FTIR does better with CO_2 , OCS , CH_4 , and C_2H_4 (all by approximately an order of magnitude). Neither technique can detect

all the gases in the mixture with the required sensitivity and selectivity, but between the two techniques all the gases can be detected at the 100 ppm level or better.

Other factors should also be considered when weighing the relative merits of the two techniques. The Raman system has a much smaller dead volume, and consequently requires far less sample. The FTIR system obtains information on all components simultaneously, and has extensive software support. While it is difficult to compare these results directly with reported literature values, it does not appear that existing state-of-the-art techniques for either Raman or FTIR spectroscopy could hope to improve substantially on the results reported in Table I and II.

These results can be profitably compared to those obtained with mass spectroscopy techniques, however. A conventional mass spectrometer (i.e., a single quadrupole instrument) was used in monitoring species-selective kinetics in a fluidized-bed pyrolysis experiment.²⁸ In this case five gases were monitored simultaneously, with data points approximately every four seconds and LOD's on the order of 30 ppm (± 20) for the five gases examined (H_2 , CO_2 , CH_4 , C_2H_4 , and C_2H_6). The LOD's were estimated on the basis of standards; similar estimates applied to the sulfur species. Conversely, a 4-g sample of oil shale (24.8 gal/ton) pyrolyzed at the lowest temperature (460°C) produced a methane peak with $S/N \approx 100$ and a maximum concentration of $\sim 0.1\%$. Once again, the LOD for this worst case (i.e., lowest temperature) is estimated to be on the order of 20 ppm, and the kinetic decay could easily be followed with a temporal resolution of 4 s for over nearly two orders of magnitude.

Similarly, the triple quadrupole ms/ms system has a reported sensitivity for several sulfur compounds (e.g., thiophene, n-propanethiol) on the order of 1-10 ppm with a 1 s time constant.²⁹

Thus, both mass spectroscopy techniques yielded sensitivities for typical oil shale gases in complex mixtures with the required temporal resolution which were similar to or substantially better than that obtained with either Raman or FTIR spectroscopy. They also have software support similar to FTIR and exceeding what is immediately available for the Raman system. The sole salient advantage of Raman spectroscopy is the capability of doing remote, in-situ monitoring.

Consequently, the conclusion of this feasibility study was to eliminate both Raman and FTIR spectroscopy as viable, widely applicable techniques for doing oil shale gas analysis. Mass spectroscopy appears to have a definite and substantial advantage over Raman or FTIR spectroscopy for doing simultaneous multicomponent oil shale gas analysis in complex mixtures with time constants on the order of seconds and corresponding sensitivities in the order of 10 ppm or better.

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References

1. a) W. M. Tolles, J. W. Nibler, J. R. McDonald, and A. B. Harvey, Appl. Spectrosc. 31, 253 (1977); b) A. B. Harvey and J. W. Nibler, Appl. Spectrosc. 14, 101 (1978).
2. D. R. Siebert, G. A. West, and J. J. Barrett, Appl. Opt. 19, 53 (1980).
3. A. Owyong, Opt. Commun. 22, 323 (1977).
4. W. M. Tolles and R. D. Turner, Appl. Spectrosc. 31, 96 (1977).
5. B. F. Levine and C. G. Bethea, IEEE J. Quantum Electron. QE-16, 85 (1980).
6. D. E. Diller and R. F. Chang, Appl. Spectrosc. 34, 411 (1980).
7. J. Laane and K. Krishnan, "Detection of Environmental Pollutants using Laser Raman Spectroscopy," available from NTIS, #AD-776290 (1973).
8. C. K. N. Patel, Science 202, 157 (1978).
9. S. D. Bloom, R. C. Harney, and F. P. Milanovich, Appl. Spectrosc. 30, 64 (1976).
10. A. C. Eckbreth, P. A. Bonczyk, and J. F. Verdieck, Prog. Energy Combust. Sci. 5, 253 (1979).
11. J. A. Sullivan and R. J. Jensen, AICHE Meeting, Houston, TX (April, 1981), LA-UR-81-131.
12. a) J. O. Lephardt and R. A. Fenner, Appl. Spectrosc. 34, 174 (1980); J. O. Lephardt and R. A. Fenner, Appl. Spectrosc. 35, 95 (1981).
13. W. L. Maddox and G. Mamantov, Anal. Chem. 49, 331 (1977).
14. J. O. Lephardt and G. Vilcens, Appl. Spectrosc. 29, 221 (1975).
15. S. A. Leibman, D. H. Ahlstrom, and P. R. Griffiths, Appl. Spectrosc. 30, 355 (1976).
16. A. W. Mantz, Appl. Spectrosc. 30, 459 (1976).
17. D. A. Saperstein, Anal. Chem. 52, 1565 (1980).
18. P. L. Robin and P. C. Rouxhet, Geochim. Cosmochim. Acta 42, 1341 (1978).

19. P. R. Solomon and F. P. Miknis, Fuel 59, 893 (1980).
20. R. S. Brown, D. W. Hausler, and L. T. Taylor, Anal. Chem. 52, 1511 (1980).
21. a) P. C. Painter, R. W. Snyder, M. Starsinic, M. M. Coleman, D. W. Kuehn, and A. Davis, Appl. Spectrosc. 35, 475 (1981); b) P. C. Painter, S. M. Rimmer, R. W. Snyder, and A. Davis, Appl. Spectrosc. 35, 102 (1981).
22. P. C. Painter and M. M. Coleman, "The Application of Fourier Transform Infrared Spectroscopy to the Characterization of Coal and Its Derived Products," Digilab FTS/IR Notes No. 31 (1980).
23. P. R. Solomon, Adv. Chem. Ser. 192, 95 (1981).
24. a) P. R. Solomon, ACS Div. Fuel Chem. Preprints 24, 154 (1979); b) *ibid*, 184.
25. P. R. Solomon and M. B. Colket, Fuel 57, 749 (1978).
26. M. D. Erickson, S. E. Frazier, and C. M. Sparacino, Fuel 60, 263 (1981).
27. P. L. Hanst, A. S. Lefohn, and B. W. Gay, Appl. Spectrosc. 27, 188 (1973).
28. J. H. Richardson, E. B. Huss, L. L. Ott, J. E. Clarkson, M. O. Bishop, J. R. Taylor, L. F. Gregory, and C. J. Morris, UCID, in preparation (July 1982).
29. R. W. Crawford and C. M. Wong, ASMS Meeting, Honolulu, Hawaii (June, 1982).

Table I. Summary of Raman results.

Compound	Raman shift (cm ⁻¹)		LOD (ppm)	
	Exp'tal	Lit.	Syn. mix	FA gas
H ₂	591	593	470	500
CO	2144	2157	350	150
CO ₂	1392	1388	250	100
OCS	869	858	30	---*
CH ₄	2921	2917	70	50
C ₂ H ₄	1346	1342	180	60
C ₃ H ₈	2888	2888	650	300
H ₂ S	2614	2614	100-350**	100
CH ₃ SH	2573	2573	20	11
C ₄ H ₄ S	817	817	70	---*

*Not present in FA gas above LOD.

**Uncertainty due to mass spectroscopic analysis.

Table II. Summary of FTIR results.

Compound	Absorption (cm ⁻¹) Exp'tal	LOD (ppm) Syn. mix
H ₂	---	---
CO	2169	400
CO ₂	2340	20
OCS	2062	4
CH ₄	3018	10
C ₂ H ₄	949	20
C ₃ H ₈	1440	400
H ₂ S	2615	4000
CH ₃ SH	1483	4000
C ₄ H ₄ S	712	40

Figure Captions

Figure 1. Schematic of Raman system.

Figure 2. Raman calibration curve for methane. Approximately 6.8 W at 514.5 nm, 6 cm⁻¹ slitwidth, 1:1 mixture of nitrogen:methane progressively pumped down.

Figure 1

Figure 2

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