

TABLE II. Absorbances of CO₂, CH₄, and NH₃ as a function of temperature of the cylinder.

Day	CO ₂			CH ₄			NH ₃		
	30°C	40°C	50°C	30°C	40°C	50°C	30°C	40°C	50°C
1	0.006	0.480	0.054			0.017			
2	0.031	0.566	0.106			0.043			
3	0.058	0.542			0.046	0.478			
4	0.042	0.511	0.666		0.084	0.568			
7	0.208	0.388	0.434		0.059	0.454		0.087	
8	0.034	0.335	0.541		0.079	0.301		0.092	
9	0.301	0.335	0.752		0.086		0.088	0.094	0.072
10	0.024	0.306	0.467		0.086	0.073	0.088	0.094	
11	0.029	0.244	0.681		0.066	0.078	0.090		
14	0.024	0.139	0.102		0.045	0.051		0.028	
15		0.097	0.069		0.038	0.042			
16		0.105	0.058		0.048	0.063			
17		0.103			0.052				
18		0.098			0.036				
21		0.174			0.059				

composition gases was studied when the controlled sanitary landfill was maintained 30, 40, and 50°C and the soil layers were saturated with water but not to the point of becoming muddy, i.e., wet soil layers. The nature of these gases was also studied at 30°C using dry soil layers in the cylinder.

The decomposition gases from the cylinders containing wet soil layers were the same at 30, 40, and 50°C. That is, the infrared spectra indicated the presence of H₂O, CO₂, NH₃, and CH₄ at all temperatures (Table I). However, the rates at which the gases evolved were temperature-dependent. The gases were identified by comparison with a catalog of infrared spectra of various gases.⁴ Analysis for ammonia gas was not reported in previous analytical studies of the gases from sanitary landfills.¹⁻³

The absorbances of CO₂, CH₄, and NH₃ gases were measured at different times with the cylinder maintained at 30, at 40, and at 50°C. The results of these studies are shown in Table II. Methane gas is not indicated in Table II for the cylinder at 30°C. At this temperature, CH₄ was not observed until the 70th day.

The decomposition gases from a cylinder containing dry soil layers and maintained at 30°C were also analyzed by infrared spectroscopy over a period of time. The major change in the gases due to the use of dry soil instead of wet soil is that N₂O is observed in the infrared spectra of the gases recorded between the 17th and 24th days of decomposition. The presence of N₂O is indicated by an absorption band located near 2220 cm⁻¹ of the spectrum.⁴ Further, no ammonia gas was observed. The presence of CH₄ was not observed until after the 70th day.

The results of this study indicate that infrared spectroscopy can be a useful analytical tool in the analysis of the decomposition gases of sanitary landfills. The presence of NH₃ gas or N₂O gas, depending on the condition of the soil, would be difficult to ascertain quickly by other conventional means and with such simple sampling procedures. Further, simultaneous qualitative and quantitative analysis may be performed on a sample. The availability of commercial portable gas analyzers permits on-site analyses for the decomposition gases of sanitary landfills.

1. California State Water Pollution Control Board, "Investigation of Leaching of a Sanitary Landfill," Publication 10 (1954).
2. R. C. Merz and R. Stone, *Public Works* **95**, 84 (1964).
3. California State Water Quality Control Board, "In-Site Investigation of Movements of Gases Produced from Decomposing Refuse," Publication 31 (1965).
4. R. H. Pierson, A. N. Fletcher, and E. St. Clair Gantz, *Anal. Chem.* **28**, 1218 (1956).

Fourier Transform Infrared Determination of Parts per Billion of Oxygen in Silicon

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Previous work on oxygen in silicon resulted in producing an infrared calibration curve based on gas fusion analysis¹. This calibration curve was also compared with an activation analysis method.² The normal spectrometric technique employs a double beam grating spectrophotometer and a 1-cm polished silicon sample and reference slices.³ The silicon lattice band at 1100 cm⁻¹ overlaps the silicon-oxygen vibration band at 1107 cm⁻¹. Thus, to measure the baseline accurately it is necessary to have an oxygen-free silicon in the reference beam. The lattice band is ratioed out of the spectra, and only the oxygen-silicon vibration band appears. Using 1-cm thick sample and reference slices a limit of

detection of 50 ppb atomic is obtained. The 1-cm thickness used is the maximum possible; the lattice absorption band absorbs sufficient energy for greater thickness to degrade the signal-to-noise ratio. The poor signal-to-noise ratio for thicker samples results in meaningless results when a spectral scan is run.

Since the oxygen content of many gas float-zoned crystals ranges between 300 ppb atomic and an undetectable 50 ppb atomic, it has become necessary to improve the lower limit of detection. Low temperature infrared spectroscopy with the grating spectrophotometer will give an improvement in detection limit.⁴ The factor of 5 or 10 improvement is paid for by increased run time and special sawing of crystals to fit the cryostat. Large scale measurement of crystals is thus not desirable under these conditions.

The recent advances in Fourier Transform Spectrophotometry presents us with a simple solution to the measurement problem. With an instrument of this design we have achieved a substantial improvement in detection limit without adding extra costs for sample preparation and instrument time.

Fig. 1 is the spectrum of an oxygen-containing silicon slug, 2 cm in thickness, computer-ratioed against a reference 2-cm thick oxygen-free silicon slug as obtained on a Digilab FTS-14. The Digilab FTS-14 was used in the STORE/RATIO single beam mode.⁵ Both sample and reference spectra were measured by coadding 500 scans using a spectral resolution of 16 cm⁻¹ with a triangular apodization function and 4 cm⁻¹ with a boxcar apodization function. The triangular apodization function further decreases the spectral resolution to about 20 cm⁻¹, but with an improved signal-to-noise ratio. The trade-off in resolution for increased signal-to-noise ratio presents no problem here because of the relatively large half-band width (32 cm⁻¹) of the asymmetric Si-O stretching vibration at 1107 cm⁻¹. A small uncertainty in absolute transmission amounting to less

than $\pm 0.4\%$ ($\pm 1.1\%$ absorbance) was noted in going from a boxcar to triangular apodization function at 16 cm⁻¹ resolution. This should not alter the results reported here since all measurements are referred to a reference run under identical conditions.

The computer scale expanded trace of the Si-O band shows the peak height of the band at 0.999 %T and the baseline at 1.023 %T. This calculates as 122 ppb atomic oxygen compared with the value 124 ppb atomic oxygen obtained from a low temperature scan on a Beckman IR-12. The signal-to-noise ratio in Fig. 1 is estimated as $\sim 30/1$. If the lower limit of detectability is assumed to be twice the noise level, then one would conclude that for a 2-cm thick slug, the lower limit of detectability for oxygen is about 8 ppb atomic. This figure, 8 ppb atomic oxygen, is in the same range as the estimated lower limit of detectability for oxygen using low temperature techniques with a grating spectrophotometer. However, there are time-saving features associated with the FTS-14 analysis. The crystals do not have to be specially cut to fit into a cryostat. The total run time is approximately 10 min per sample. The system was found stable enough so that the same reference (run time 10 min) could be used over a period of several hours.

1. J. A. Baker, *Solid State Electronics* **13**, 1431 (1970).
2. C. Gross, G. Gaetano, T. N. Tucker, and J. A. Baker, *J. Electrochem. Soc.* **119**, 926 (1962).
3. ASTM Part 8 F-120.
4. B. Pajot, *Solid State Electronics* **12**, 923 (1969).
5. M. J. D. Low and H. Mark, *J. Paint Technol.* **42**, 265 (1970).

Pressure-Temperature Relationships for Fe(II) Complexes of 1, 10-Phenanthroline and 2, 2'-Bipyridine*

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The complexes of the type Fe(phen)₂X₂ and Fe(bipy)₂X₂ (phen = 1,10-phenanthroline, bipy = 2,2'-bipyridine) exist in high spin states (X = Cl⁻, Br⁻,

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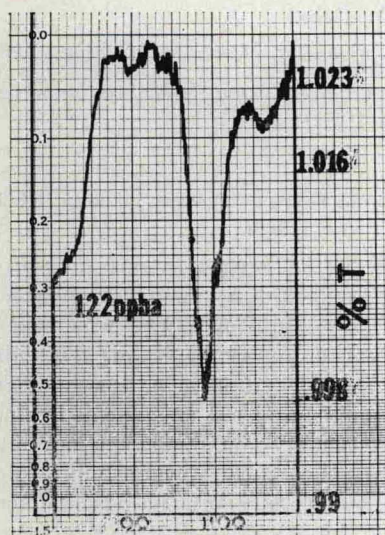


FIG. 1. Scale-expanded spectrum of 122 ppb atomic oxygen in silicon computer ratioed against an oxygen-free silicon slug run at 4 cm⁻¹ resolution.