



Project Summary

Methods of Chemical Analysis for Oil Shale Wastes

J. Wallace, L. Alden, F. S. Bonomo, J. Nichols, and E. Sexton

Several methods of chemical analysis are described for oil shale wastewaters and retort gases. These methods are designed to support the field testing of various pollution control systems, and emphasis is therefore placed on methods which are rapid and sufficiently rugged to perform well under field conditions.

Ion chromatography has been developed as a technique for the minor non-carbonate inorganic anions in retort water, including SO_4^{2-} , NO_3^- , S^{2-} , SCN^- , and total sulfur (S). Acetate, Cl^- , SO_3^{2-} , NO_2^- , and PO_4^{3-} can be observed with this technique but cannot necessarily be separated if present simultaneously.

The method recommended for sulfide is a potentiometric titration with Pb(II) . SCN^- , $\text{S}_2\text{O}_3^{2-}$, SO_4^{2-} , Cl^- , CO_3^{2-} , NH_3 , and OH^- were shown not to interfere with this technique. The freezing point depression is used to determine the total solute content in retort waters, a test which can be considered analogous to the standard residue test.

Three methods are described for the determination of total ammoniacal nitrogen in retort wastewaters: (1) a modified ion selective electrode technique; (2) an optical absorption technique; and (3) an ion chromatographic technique. The latter technique is recommended for routine monitoring of retort water, although the relative advantages of each are discussed in the report.

Total sulfur in retort gas is determined by combusting the gas in a continuously flowing system, whereupon the resulting sulfur dioxide is determined by an SO_2 monitor. Individual sulfur species in retort gas, including H_2S , COS ,

SO_2 , CS_2 , and $\text{CH}_3\text{CH}_2\text{SH}$, are determined by gas chromatography with flame photometric detection.

Potential interferences due to co-eluting hydrocarbons or other sulfur species are examined extensively.

Quality control, pH, conductivity, total inorganic carbon, and total organic carbon measurements are discussed briefly.

This Project Summary was developed by EPA's Industrial Environmental Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

The full report describes methods of chemical analysis required to adequately test the various pollution control technologies being proposed for the treatment of oil shale retort gases and wastewaters. Included in the full report are step-by-step protocols for determining important species. Supporting evidence and discussion permit the analyst to adjust the procedure to the varied sample types encountered. The report stresses methods that are rugged and rapid enough to be used during the field testing of pollution control systems.

Major and Minor Ion Detection

A type of ion exchange chromatography, referred to in the literature as suppressed ion chromatography, was used to determine major and minor anions in retort wastewaters. Originally, this method indicated the presence in retort wastewaters of very late-eluting

compounds which, because they could not be removed from the column in a reasonable time, interfered with subsequent analyses. This problem was solved with a column switching arrangement that allows the late eluters to be separated on a pre-column while the earlier-eluting compounds are separated on the main analytical column. The same valve and column configuration can be used for four different protocols: the first protocol, referred to as the majors protocol, determines SO_4^{2-} , NO_3^- , $\text{S}_2\text{O}_3^{2-}$, and SCN^- in a single run using 7 mM Na_2CO_3 as an eluent. The second protocol determines the late eluters, $\text{S}_2\text{O}_3^{2-}$ and SCN^- using an eluent of 7 mM NaCO_3 + 0.5 mg/L of SCN^- . The third protocol determines earlier eluters by using a valve switching arrangement that traps the late eluters on a pre-column, which is periodically flushed to waste. Peaks observable with this procedure include Cl^- , acetate, NO_2^- , SO_3^{2-} , NO_3^- , PO_4^{3-} and SO_4^{2-} , although not all have been successfully separated when present in the same solution. While the valving and column configuration remain unchanged, the analysts must be prepared to adjust the eluent for the various types of samples and analytes encountered. The fourth protocol measures total sulfur by oxidizing the various sulfur species present to SO_4^{2-} , which is then determined by the protocol for the early eluters.

Sulfide Detection

The determination of sulfide by potentiometric titration with Pb(II) was investigated for retort wastewaters. Thiocyanate, thiosulfate, sulfate, chloride, carbonate, ammonia, and hydroxide ions, all of which are components of retort waters, were tested as potential interferences for sulfide concentration in the range 1-1,000 mg/L and were shown to be insignificant within the normal range of interest. The titration was evaluated for precision, recovery, reliability, and ease of use, under field conditions with actual retort waters. The titration procedure was also compared to the direct calibration method with the AgS ion selective electrode to monitor the titration and a Gran's plot end point, is the preferred method of analysis.

Thermal evaporation, lyophilization, and the measurement of colligative properties were investigated as the total solute content in retort wastewaters. Of these, both thermal evaporation and lyophilization were shown to be inap-

propriate. Of the various colligative properties considered, the freezing point depression method gave the best measurement of total dissolved solutes: the total solute content is measured in units of moles/liter over the range 0.001 - 3.0 moles/liter (counting each ion separately).

Ammoniacal Nitrogen Detection

Three distinct methods were developed for the analysis of ammoniacal N in retort waters. Although the first method employs an ammonia selective electrode, it minimizes many of the problems associated with that device by maintaining the electrode in pure standard to which small amounts of sample are added. The second method, ion chromatography, separates NH_4^+ on an ion exchange column with detection by electrical conductivity. The third method involves absorption of UV radiation by ammonia in the headspace over a basic sample solution. All three methods are capable of quantitating ammoniacal N in turbid, briny, and organic-laden wastewaters; all three have notable secondary characteristics: the first method requires the least investment in equipment but is the most labor intensive and the least precise; the ion chromatographic method, readily implemented with commercially available equipment, can also measure Na and K simultaneously; the gas absorption method shows promise as the basis for an on-line, unattended monitor and is capable of distinguishing between aqueous NH_3 and NH_4^+ . The gas absorption method gives the most precise measurement, but its spectral background must be corrected to achieve accuracy.

Sulfur Detection

A method for measuring total sulfur in oil shale retort gas operates by converting the various sulfur species to SO_2 , which is then monitored by a commercially available monitor. A heated tube and a flame, respectively, were evaluated for conversion of the various individual sulfur species to SO_2 . The tube was rejected because it depended both on temperature and on the species being oxidized. The flame converted essentially 100% of the various sulfur species to SO_2 , and a full-scale device was constructed for the measurement of total sulfur in retort gas. The device was tested at an oil

shale retort, and measured total sulfur in agreement within experimental error with the sum of the individual sulfur species.

Gas chromatography with flame photometric detection was developed as a method for measuring sulfur species in retort gas. To establish the veracity of this technique, two potential problems were considered in detail. First, because hydrocarbons, a major component of retort gas, are known to quench the fluorescence of the flame photometric detector (FPD), it was necessary to determine fluorescent quenching effects in realistic retort gas. The second potential problem was the large number of sulfur species which can occur in retort gas and which must be separated from each other if an unambiguous assignment is to be made to each.

Fluorescent quenching effects were measured on two types of commercially available FPDs, a single-flame detector and a dual-flame detector. The latter exhibited no significant quenching effects over the concentration ranges of interest in retort gas. However, quenching effects for the single flame detector cannot be ruled out entirely. Although hydrogen sulfide in retort gas is usually abundant enough to minimize quenching effects, the minor species can be subject to quenching effects unless precautions are taken. These precautions include operating the detector with the air and hydrogen flows reversed and measuring peak height rather than peak area. In addition, columns are selected that minimize coelution with hydrocarbons. The single flame detector exhibited both suppression and enhancement of the fluorescent signal.

Because of the large number of sulfur species which could occur in retort gas, a single packed column could not unambiguously separate all possible species; therefore, efforts were made to locate a column which could separate the compounds of primary interest--hydrogen sulfide, carbonyl sulfide, sulfur dioxide, carbon disulfide, methyl mercaptan, and ethyl mercaptan--from each other as well as from the later eluting sulfur compounds. Several columns were evaluated for their ability to achieve this separation as well as the required separation from hydrocarbons. Columns were also tested for their ability to tolerate water vapor and the other compounds in retort gas. The best general purpose column packing for the determination of the sulfur compounds of primary interest was a Carbopack B HT

100*, although a Chromosil 310 packing would be useful for the occasional determination of thiophenes. A protocol for the primary sulfur species is described for the concentration range of 5-50,000 ppmv using a Carbopack B HT 100 column arranged in a backflush-to-detector configuration.

Other Pertinent Data

Although electrical conductivity, pH, alkalinity, and total inorganic carbon are not investigated explicitly in this study, they are discussed briefly in the full report. It is suggested that the measurement of pH and electrical conductivity with the standard conductivity cell and pH electrode, respectively, has demonstrated no obvious problems, but frequent cleaning and calibration should be expected. It is recommended that the alkalinity test be discontinued as a measurement of dissolved carbon dioxide because of interferences due to ammonia and organic acids. Dissolved carbon dioxide should instead be determined by commercially available analyzers which are also suitable for total organic carbon measurements. Precautions for the latter two measurements are discussed in the text.

*Mention of tradenames or commercial products does not constitute endorsement or recommendation for use by the U.S. Environmental Protection Agency

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The complete report, entitled "Methods of Chemical Analysis for Oil Shale Wastes," (Order No. PB 84-211 226; Cost: \$20.50, subject to change) will be available only from:

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