



# Project Summary

## Development and Evaluation of Analytical Test Procedures for Priority Pollutants

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Analytical methods were developed for the determination of cyanide and of total phenolic compounds in solid/semisolid samples of environmental importance. The approach to the problem was to: 1) select the most promising isolation and quantification methods from a literature search; 2) empirically evaluate them in order to choose the methods for further study; 3) modify and optimize the procedural steps of the methods; and 4) validate the methods by applying them to a variety of actual solid/semisolid samples. Each method consisted of two steps: isolation of the analyte and quantification of the analyte. Isolation studies were performed using radiolabeled cyanide and radiolabeled phenolic compounds to spike representative matrices.

The method which was selected for the determination of cyanide in solid/semisolid matrices involves distillation of cyanide from an acidified slurry of the sample, followed by quantification using the pyridine-barbituric acid procedure. The method which was selected for the determination of total phenolic compounds involves extraction of an acidified slurry of sample with methylene chloride. The methylene chloride is then extracted with a sodium hydroxide solution and quantified using the 4-aminoantipyrene (4-AAP) procedure.

*This Project Summary was developed by EPA's Environmental Monitoring and Support 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

Cyanide complexes are found in the wastes of many industrial processes such as electroplating, metal refining, and steel hardening. They are intermediates in polymer synthesis and are used as fumigants in produce storage. Phenolic wastes are generated by the petroleum, plastics, and organic chemical industries. Both compounds may accumulate in sediments and are taken up by aquatic plants and animals in a variety of ways.

Under the Federal Water Pollution Control Act Amendments of 1972 (Public Law 92-500), proposed discharges of dredged or fill material into navigable waters will be evaluated by the U. S. Environmental Protection Agency. The procedures developed in this study will be considered as potential avenues for obtaining analytical information concerning the material in question.

### Results

#### *Cyanide*

For the isolation of cyanide from the sample, distillation was clearly the most viable alternative. Microdiffusion, which has been used for biological samples for volatile cyanides, is severely limited by sample size requirements. Solvent extraction of cyanide from a solution of sodium hydroxide and ammonium hydroxide with hexane and with methylene chloride gave less than 1% recovery and was therefore eliminated from further consideration.

Hydrogen cyanide is distilled under aeration from an acidified slurry containing magnesium chloride. The gas passes through an absorber containing lead acetate solution in order to remove interfering sulfur compounds; then it passes into an absorber containing sodium hydroxide solution for final collection. For thick slurries resulting from high sample volume and weight, simultaneous stirring with a magnetic stirrer prevents bumping.

Radiolabeled cyanide was spiked onto several matrices which were then distilled. The distillation efficiency was followed by withdrawing aliquots for scintillation counting. The recovery of cyanide from spiked solid/semisolid samples varied with the nature of the sample matrix and the distillation time. Typically, fish tissue yielded 40% of the spike, lake bottom sediment yielded 63-86% of the spike, and sludge yielded 43-52% of the spike using a two-hour distillation period.

Seven methods for the quantification of cyanide were experimentally evaluated. Five of these were spectrophotometric methods involving the use of: 1) pyridine-barbituric acid reagent; 2) tris(1,10-phenanthroline) iron (II) reagent; 3) mercuric chloranilate reagent; 4) ammoniacal nickel chloride reagent; and 5) *N,N*-dimethylformamide reagent. The other two were: 1) an ion selective electrode method; and 2) a gas chromatographic method involving the determination cyanogen bromide after bromination of the sample.

Though the gas chromatograph is the most sensitive instrument for these analyses, the necessary preliminary solvent extraction produced an average of only 50% recovery. The pyridine-barbituric acid procedure was the next most sensitive and produced an average 97% recovery of spiked distilled water samples.

Experiments which were performed using spiked fish tissue demonstrated both the necessity of the lead acetate trap and the near quantitative recovery of spikes.

The validation study involved recovering spikes at the 2.6  $\mu\text{g/g}$  level and the 20  $\mu\text{g/g}$  level from ten solid/semisolid matrices. The matrices and the average percent recovery of the spikes are: lake bottom sediment (84  $\pm$  6%); industrial sludge (84  $\pm$  12%); industrial solid waste (94  $\pm$  11%); industrial processing slag (94  $\pm$  3%); incinerator fly ash (95  $\pm$  7%); contaminated soil (103  $\pm$  12%); fish tissue (94  $\pm$  6%); microinvertebrates (shrimp) 92  $\pm$  6%; algae (76  $\pm$  1%); and vegetation (84  $\pm$  10%).

## Phenol

For the isolation of phenolic compounds from the sample, solvent extraction with methylene chloride was selected as the most successful alternative. Steam distillation, which is the recommended method for aqueous samples, gave near quantitative recovery of phenol, but almost no recovery of *para*-nitrophenol and of 2,4,5-trichlorophenol. While they are potential separation methods, liquid chromatography and carbon adsorption techniques are of limited capacity and require further study. Soxhlet extraction with methylene chloride appears to be almost as efficient as extraction with stirring only. Further study of this alternative may produce improvement.

The acidified and blended sample slurry is extracted with methylene chloride which in turn is extracted with diluted sodium hydroxide solution for the quantification step.

Radiolabeled phenolic compounds were spiked onto several matrices and were then extracted. The extraction efficiency was determined by scintillation counting of aliquots of the methylene chloride. After two hours of stirring, the methylene chloride yielded from 72-98% of three radiolabeled phenolic compounds which were spiked onto fish tissue, lake sediment and sludge.

Three methods for the quantification of total phenolic compounds were evaluated by performing seven determinations on spiked aqueous samples. The 4AAP method, the 3-methyl-2-benzothiazolinone hydrazone colorimetric method (MBTH), and the bathochromic shift procedure (two variations - one using a laboratory spectrophotometer and the other using a commercial ultraviolet ratio spectrophotometer) were evaluated. The sensitivity, range, precision, and accuracy were measured. The commercial ultraviolet ratio spectrophotometer was the most sensitive and the laboratory spectrophotometer was least sensitive.

The 4-AAP method was selected because:

1. It has been shown to work on a wide variety of environmentally important aqueous matrices.
2. The results can be compared to an abundance of accumulated data.
3. Phenolic mixtures determined by the two methods would most likely not be linearly related since the substituent effects are not quantitatively related.
4. The ultraviolet ratio spectrophotometer is not available in most laboratories where analyses on solid/semi-

solid matrices will be performed.

5. The sensitivity of the 4AAP method is already more than adequate, thus the advantage of the ultraviolet ratio spectrophotometer is minimal.

The validation study involved recovering spikes at the 0.80  $\mu\text{g/g}$  level and the 4.0  $\mu\text{g/g}$  level from ten solid/semisolid matrices. The matrices and the average percent recovery of the spikes are: lake bottom sediment (75  $\pm$  5%); industrial sludge (55  $\pm$  4%); industrial solid waste (71  $\pm$  13%); industrial processing slag (36  $\pm$  10%); fish tissue (26  $\pm$  3%); microinvertebrates (shrimp) (39  $\pm$  5%); algae (34  $\pm$  10%); and vegetation (42  $\pm$  9%).

## Preservation

A concurrent preservation study was performed. For cyanide, three methods were studied: 1) storage at less than 0°C; 2) storage at 4-6°C; and 3) storage at 4-6°C with sodium hydroxide addition. For phenol, three methods were studied: 1) storage at less than 0°C; 2) storage at 4-6°C; and 3) storage at 4-6°C with phosphoric acid and copper sulfate addition.

The best methods for preserving cyanide are freezing in dry ice and storage at 4-6°C after the addition of sodium hydroxide. In this study, the former method was used in order to avoid the difficulties encountered when using sodium hydroxide solution in the field.

Freezing in dry ice was clearly the superior method for preserving phenolic compounds. The other alternatives for preserving phenolics allowed extremely rapid deterioration. For verification, cyanide-containing sludge from a chemical processing manufacturer and phenol-containing soil which had been contaminated by a chemical manufacturing plant were stored at less than 0°C for up to 16 days. Periodic analyses by the selected colorimetric procedures showed virtually no loss of analyte.

This project summary was prepared by Daniel F. Bender of the U. S. Environmental Protection Agency from the report prepared by Carolyn Monteith of the Gulf South Research Institute. Daniel F. Bender is the U.S. EPA Project Officer. Carolyn Monteith is the GSRI Project Manager.

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*The complete report, entitled "Development and Evaluation of Analytical Test Procedures for Priority Pollutants," (Order No. PB 83-166 181; Cost: \$13.00, subject to change) will be available only from:*

*National Technical Information Service  
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