

STUDY TITLE: Trace Metals Quality Control Analyses

REPORT TITLE: Quality Control for MAFLA IV and South Texas II Investigations

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BACKGROUND: A comprehensive quality control program was conducted in support of the Mississippi, Alabama, and Florida (MAFLA) Outer Continental Shelf (OCS) Monitoring Study and South Texas OCS Baseline Program. Such quality control programs are needed in order to be able to make comparative assessments of chemical analyses from different laboratories and for individual studies.

OBJECTIVE: To provide trace metals analyses and quality control for samples of suspended particulate matter, biota, and sediment from the MAFLA Monitoring Study and South Texas OCS Baseline Program.

DESCRIPTION: A total of 241 samples including 10 suspended particulate, 31 zooplankton, 19 paint chip samples, 75 sediment, and 106 epifauna samples were analyzed for quality control trace metal testing. Suspended particulates, zooplankton, epifauna, and sediments were analyzed from the South Texas OCS Baseline Program. Zooplankton, paint chips, sediments, and epifauna were tested from the MAFLA area, and sediments and epifauna from the MAFLA Rig Monitoring Study. All samples were measured for cadmium, copper, lead, nickel, and vanadium with additional analyses on specific samples for barium, iron, and zinc.

Analytical methodologies which were investigated included hot nitric acid digestion, liquid fire digestion, and a 10-day procedure based on the principle of the Parr bomb. Testing of the procedures was accomplished by digesting aliquots of four biota pools (i.e., shrimp, oysters, sand dollars, and flounder). Based on results of an accuracy test, the 10-day procedure was selected for digestion of epifauna and zooplankton samples. Flame and flameless atomic absorption spectrophotometry (AAS) were used to make the metals determinations.

SIGNIFICANT CONCLUSIONS: Average concentrations of cadmium and copper in zooplankton samples tended to be higher in the MAFLA area while chromium, lead, and vanadium were higher in South Texas. Nickel levels were similar in the two areas. Concentrations of these metals in suspended particulate samples were generally two or more orders of magnitude less than those in the zooplankton. Metals concentrations in epifauna samples were generally lowest in South Texas, intermediate from the MAFLA Rig Monitoring Study, and highest in the MAFLA area.

Sediment samples in the South Texas, MAFLA, and MAFLA rig monitoring areas gave similar results with a few exceptions. Barium was lower in the MAFLA area as compared to the other two study sites. Chromium was higher in the rig monitoring samples, and vanadium was lower in the MAFLA area.

Good agreement was reached between the measured and actual concentrations in reference samples received from the National Bureau of Standards (NBS).

STUDY RESULTS: Suspended particulate matter samples were all obtained from the South Texas baseline area. Metals determinations were made for vanadium, cadmium, lead, nickel, copper, chromium, and zinc.

In analyzing biota, several experiments were conducted. A hot nitric acid digestion procedure was attempted in the first experiment which gave poor results and was lengthy. Good agreement was obtained on NBS standard reference materials but poor precision was obtained on shrimp pool samples. Precision was better for Food and Drug Administration (FDA) oysters and NBS tuna than for the shrimp.

Experiment two was designed to determine whether a 32-h acid digestion was required for accurate analysis. Analyses for cadmium, chromium, lead, and nickel did not demonstrate sufficient sensitivity or reproducibility to provide comparable time-dependent data. Copper, iron, and zinc determinations suggested that the optimum digestion time was 8 h.

In experiment three, another digestion method was attempted because of poor results with the nitric acid digestion. This digestion involved a perchloric acid-nitric acid procedure. Poor results were obtained with this method which included lack of precision and accuracy. In addition, the method was hazardous for use with biota samples and was therefore abandoned.

In the fourth experiment, a Parr bomb principle was employed to test digestion efficiency. The actual procedure employed was the 10-day procedure which used

pressure development by the action of nitric acid on the biota. The procedure gave the best precision of all the methods tested and gave good recovery of spikes for all metals tested, with the exception of zinc. A follow-up experiment was designed to determine if the 10-day nitric acid procedure could provide accurate data for an NBS reference standard. Observed precision with the method was good.

Sufficient sample volume for zooplankton analysis was provided only for the South Texas region. Precision in the samples was very good for all trace metals of interest and the recovery of spikes was good. This indicated that the analyses for zooplankton were in control. In South Texas samples, only copper and zinc were present in sufficient concentrations to be detected by flame AAS. In the MAFLA area samples, the majority of the trace metals analyzed could be detected by flame AAS. Cadmium, chromium, lead, nickel, and vanadium required flameless AAS. A graphite furnace was used for all trace elements except copper and iron in the MAFLA Rig Monitoring Study. Vanadium and chromium could be detected in most of these samples. Percent recovery of spikes in these samples ranged from 86% to 95%.

Partial and total digestion methods were attempted for sediment samples. The partial method used nitric and hydrochloric acids for leaching of metal content, whereas the total method used hydrofluoric and perchloric acids. Comparison of the two methods showed similar values for copper, lead, nickel and zinc. Chromium, vanadium, and especially barium were higher in the total digestion samples. Precision and accuracy of the two techniques were similar.

STUDY PRODUCT: McKown, M. M. and J. G. Montalvo. 1976. Quality Control for MAFLA IV and South Texas II Investigations. A final report by the Gulf South Research Institute for the U.S. Department of the Interior, Bureau of Land Management Gulf of Mexico OCS Office, New Orleans, LA. NTIS No. PB80-216302. Contract No. 08550-CT5-49. 189 pp.