Appendix I

IAEA-085 AND IAEA-086 INTERCOMPARISON STUDY ON THE DETERMINATION OF METHYLMERCURY, TOTAL MERCURY AND OTHER TRACE ELEMENTS IN HUMAN HAIR

Information Sheet

Description of the Material

The intercomparison materials IAEA-085 and IAEA-086 have been prepared from human hair; IAEA-085 represents hair with an elevated level of methylmercury and IAEA-086 contains a low level of mercury. Ten kg of human hair were collected and donated to the Agency for preparation of these materials. The material had been previously cut into uniform (1 cm) lengths, and cleaned with acetone and deionized water following the procedure developed by IAEA [1]. The material was split into two portions, each approximately 5 kg, and was radiation sterilized at 50 kGy. One portion (5 kg) was labeled with methylmercury using an established procedure [2] to achieve an elevated level of methylmercury. Both the labeled and unlabeled portions of the hair were cryogenically homogenized using the stainless steel "CryoPalla" mill at the KFA-Jülich Specimen Bank facility [3]. The hair was subjected to consecutive millings, until approximately 70% of each material was below 0.071 μm grain size. We refrained from removing the larger particles to avoid excessive contamination during sieving (it is also assumed that the larger particles prevent agglomeration of the powder).

The materials were then bottled, with 750 units of 5 g each, for IAEA-085, and IAEA-086, respectively. The materials were sterilized in the bottles at 12 kGy using a ^{60}Co Source. One bottle of each material is being distributed to each participant in the intercomparison.

Scope of the Study

The aim of the study is to evaluate the accuracy with which the participating laboratories are determining mercury and methylmercury in hair. For this purpose the results on the reported concentrations will be statistically evaluated and most probable values will be determined. Potential bias in procedures or laboratory results will be reported to the participants. Of course, all results will be treated anonymously, and only laboratory codes will be used throughout the study. Participants will be informed only of their own laboratory code.

The participants are requested to determine total mercury and methylmercury as primary goals; however, additional trace element analyses would also be welcome. All participants are requested to make at least three, but preferably six independent determinations for each element or species in each material. Homogeneity for mercury has been established down to the 10 mg level, however, samples sizes of 50-100 mg are recommended.

Following statistical evaluation of the intercomparison data, a report containing these results will be issued and sent to the participants. After satisfactory evaluations have been completed, these materials will be made available for use by any laboratory that is interested in quality assurance in population monitoring for total mercury and methylmercury.

Analytical Quality Control

Procedures of good laboratory practice (GLP) and laboratory quality assurance should be strictly applied to these analyses. The practice of quality control with certified reference materials is highly recommended. AQCS is unable to provide free of charge an additional quality assurance material for use in this intercomparison; however, BCR-CRM-397 human hair is certified for total mercury, and the IAEA-350, Tuna Homogenate, is certified for methylmercury, as well as for total mercury. Both of these CRMs are certified for additional selected trace elements. The analysis of one of these materials, or another suitable QA material, should be appropriately interfaced with the determinations on the intercomparison materials and the same procedures must be applied. The number of QA determinations should be similar to the number of actual determinations in the intercomparison materials. The results of the analyses of the QA material(s) should be reported along with the intercomparison materials on the forms and diskette provided (see Reporting of Results, below).

AQCS recommends for quantitation the use of physical principles (through fundamental constants and parameters) or primary comparator standards such as quantitative solutions made form pure metals or compounds. Reference materials are in most instances not suitable for standardization and should only be used to overcome the lack of standards or other means for quantitation for some of the elements. All uncertainties of such secondary means must be propagated to the results. Unfortunately, AQCS does not have the resources to provide primary standards.

Moisture Determination

All results are to be reported on a dry weight basis. For the determination of water content, a 250 mg portion of each material should be taken at the time of analysis and

lyophilized in a freeze dryer for 48 hours. Alternately, if a freeze-drier is not available, the portion may be dried at 80 °C for 24 hours. The analytical results are to be corrected for the determined moisture loss. For reference, please include the results of the moisture determination in the reporting form.

Reporting of Results

The results, based on dry weight, (for IAEA-085, IAEA-086, and an appropriate Quality Assurance material) should be reported to AQCS both on the Reporting Forms and on the computer diskette provided with the intercomparison materials. Please list the results for methylmercury and total mercury first, followed by any additional elements that may be determined. The results for methylmercury should be reported in mg/kg, expressed as mercury. Please also indicate the appropriate unit (μg/kg, mg/kg, etc.) for each determinant, and continue the listing with the results for the control material(s). When reporting results for the quality assurance materials, give the reference material - number in the first field of entry; *e.g.* BCR-CRM-397:Hg.

Results should include an estimate of a combined uncertainty (in the same unit, not % relative) for each determination. Estimated uncertainties in an analytical measurement consist of components which can be grouped into categories according to the way in which their value is estimated:

A: those which are evaluated by applying statistical methods to a series of repeated determinations,

B: those which are evaluated by other means.

The components are expressed in terms of estimates of variance (*e.g.* s^2 or σ^2). The combined uncertainty is characterized by the numerical value obtained by applying the usual method for the combination of variances. The combined uncertainty and its components are expressed in the form of standard deviations.

Various components which make up the total uncertainty can typically include:

a) reproducibility of measurement;
b) uncertainty in calibration;
c) bias or drift of measurement;
d) uncertainties in sample preparation (mass, dilution, *etc.*);
e) uncertainty of blank;
f) uncertainty in instrument readings (*e.g.* peak integration).

This is not an exhaustive list. It should be noted that the uncertainties listed above as examples may consist of uncertainties of both category A and B. The limit of detection should also be included for each determinant for the determined concentrations and values below the limit of detection.

A classification of the analytical procedures used (*e.g.*: acid digestion (HNO_3/HF)-liquid/liquid extraction (aqu./CCl_4/aqu.) - ETAAS, or: none-none- INAA) should be listed for each determinant on page 5. A summary description of the applied procedure including relevant reference should be given on page 6. Please use copies of the forms if more space is required.

On the DOS-formatted computer diskette, spreadsheet files have been provided both in EXCEL (XLS) and in Lotus WK1 format. If you do not have access to a spreadsheet programme, please provide the data in a TAB-DELIMITED text format (.TXT) following the column format of the example reporting form. By providing your data both in hard copy and on diskette, you will greatly facilitate our evaluation and avoid possible transcription errors.

The deadline for reporting of results is 31 November 1994. Any results received after that date will still be of interest to us, but it may not be possible to include them in the first report.

REFERENCES:

[1] CORTES TORO, E., DE GOEIJ, J.J.M., BASCO, J., *et al.*, The Significance of Hair Mineral Analysis as a Means For Assessing Internal Body Burdens of Environmental Pollutants: Results From An IAEA Co-Ordinated Research Programme, J. Radioanal. Nucl. Chem., **167** (1993) 413-421.

[2] KRATZER, K., BENES, P., SPEVACKOVA, V., The Study of Chemical Forms of Mercury in Human Hair and Other Bio-Environmental Samples, In: Report on the Second RCM on Assessment of Environmental Exposure to Mercury in Selected Human Populations as Studied by Nuclear and Other Techniques, IAEA, NAHRES-13, (1992) 25-31.

[3] SCHLADOT, J.D., BACKHAUS, F., Preparation of Sample Material for Environmental Specimen Banking Purposes - Milling and Homogenization at Cryogenic Temperatures, In: Progress in Environmental Specimen Banking, (S.A. Wise, R. Zeisler, G.M. Goldstein, Eds.) NBS Spec. Publ. 740 (1988) 184-193.