

Committee on Residues and Related Topics

Metals and Other Elements

MILAN IHNAT

Pacific Agri-Food Research Centre, Summerland, Agriculture and Agri-Food Canada, Summerland, British Columbia, V0H 1Z0, Canada, Tel: +1-250-494-6411, Fax: +1-250-494-0755, E-mail: ihnatm@agr.gc.ca

Summary

This is the 10th report of the General Referee covering developments during the past year, presenting selected reports and concluding with recommendations for consideration by the Methods Committee on Residues and Related Topics.

Selected Topics

Atomic Absorption Spectrometry

Study Director Milan Ihnat submitted a report summarizing progress in 2 related areas, Atomic Absorption Spectrometry and Reference Materials related to his Study Director topic.

Preparation of a comprehensive review on "Flame Atomic Absorption Spectrometric Methodologies for Food Analysis" in progress has benefitted from a survey conducted regarding methods used for the determination of major, minor, and trace elements in feedstuffs and related biological materials in a related undertaking. Challenges posed by analytical endeavours in general, as well as challenges posed by some difficult-to-measure elemental analytes, were noted. Attributes of currently available definitive, reference, routine, field, official, unofficial, and recommended methods from AOAC INTERNATIONAL and other method-developing agencies and standards organizations as well as other sources were reviewed as a basis for the formulation of method recommendations. This review will offer guidance for the development of a unified, comprehensive, multielement flame atomic absorption scheme of analysis of foods for a range of major, minor, and trace elements. Development of the unified method and full scale collaborative study based on it are proposed for 2002–2003.

Extension of Method Development to Atomic Emission and Mass Spectrometry

Among the deficiencies in Official methods of analysis, 2 have a bearing on current research/development activities by the Study Director: (1) the existence of many different methods or many variants of the same method for the same element developed for different commodities leading to duplication of methods; (2) the application of methods, that are, or can be considered to have multielement capability, to the determination of only one, or at best, a small number of elements. This is particularly the case with analytical determinations based on

atomic absorption spectrometry. Proliferation of atomic spectrometric analytical methods has resulted in multiple and overlapping developments in official, reference, and recommended methods in the literature, but still has left gaps with respect to unified approaches applicable, simultaneously, to many matrixes and elements. Clearly this demonstrates a need for consolidation of atomic spectrometric methods into multielement ones for efficient cost-effective analysis; this has led to the current work on development of a unified scheme for flame atomic absorption spectrometry.

In the author's research on the uptake of elements from waste-amended soils by agricultural crops, there is a requirement for extensive multielement determinations on plant, soil, and waste materials for a wide range of major, minor, and trace nutrient and toxicant elements. Three complementary atomic spectrometric techniques are being employed to provide analytical data for the relatively large number of elements desired. Firstly, reliance is being placed on direct determinations by flame atomic absorption spectrometry on solutions prepared by acid digestion. Efforts are underway to fine tune and adapt this technique to current needs and concurrently extend it to be more broadly applicable. At the normally expected concentrations in foods and feedstuffs, a strong potential exists for the following elements to be amenable for measurement by methods based on direct flame atomic absorption spectrometry: Al, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, Rb, Sr, Zn. The list of elements determinable by atomic absorption can be augmented by inclusion of additional steps such as complexation-solvent extraction and concentration by precipitation to separate elements of interest from interfering matrix constituents and to concentrate them prior to introduction to the flame spectrometer. Electrothermal atomic absorption (graphite furnace, tantalum strip) with or without analyte separation/concentration is another variant that can significantly extend capability. These modifications offer enhanced potential but also incur more analytical procedural complexity and neither of these techniques are being presently pursued; development is being restricted to the simpler flame version technique.

Secondly, in addition to use of atomic absorption, complementary techniques of inductively coupled plasma atomic emission spectrometry and inductively coupled plasma mass spectrometry are being employed to provide analytical data on elements for which adequate data cannot be provided by flame atomic absorption. It thus appears logical to consider extension of method development to include inductively coupled plasma atomic emission spectrometry and inductively coupled plasma mass spectrometry, 2 excellent techniques. These 2 techniques have advantages over flame atomic absorption by being truly simultaneous, multielement techniques and by possessing the capability to measuring elements not typically amenable to determination by flame atomic absorption. A sig-

nificant additional advantage of mass spectrometry is its excellent detectivity, thus ability to measure elements at very low concentration levels indeed. Fine tuning of sample decomposition and analytical parameters, desirable for optimum performance and data output, is expected to lead unified, official/recommended methods for foods, feedstuffs, and by extension, for biological materials in general, based on, the 3 most common, widely-used atomic spectrometric techniques for elemental determinations: flame atomic absorption, inductively coupled plasma atomic emission and inductively coupled plasma mass spectrometries. This will make available, comprehensive methods for a wider range of elemental analytes in biological materials than currently found in the official literature, covering elements such as Al, As, B, Ba, Ca, Cd, Co, Cr, Cu, Fe, L, La, Mg, Mn, Mo, Ni, P, Pb, Rb, S, Se, Sn, Sr, Th, Ti, U, V, and Zn. Availability of validated, unified, comprehensive approaches employing these 3 atomic spectrometric techniques, covering much of the elemental periodic table, will contribute significantly to the provision of analysts in food, feed, clinical, environmental, and other disciplines, with the tools to cover many, if not most, of their elemental analytical requirements.

Thus 2 new, complementary topics (Elements in Foods, Feeds, and Biological Materials by Inductively Coupled Plasma Atomic Emission Spectrometry and Elements in Foods, Feeds, and Biological Materials by Inductively Coupled Plasma Mass Spectrometry) are being proposed to the General Referee and the Committee.

Reference Materials

Scientific and technical information relating to the 12 Agricultural-Food Reference Materials for elemental data analytical quality control, developed by the Study Director in a collaborative venture between Agriculture and Agri-Food Canada (Ottawa) and the National Institute of Standards and Technology (NIST; Gaithersburg, MD), continues to be disseminated. The Study Director continues to play roles within the Technical Division on Reference Materials as, Member-at-Large, Liaison to the Methods Committee on Feeds, Fertilizers, and Agricultural Related Topics, and member of the Reference Materials Methods Matching Committee. A Technical Report, comprehensively documenting the entire Reference Material development venture, is in preparation. A report, related to Reference Materials, was presented and published (1).

Selected Study Director Topics

Graphite Furnace Atomic Absorption Spectrometry

Method Advisor Robert W. Dabeka reported that there was no opportunity to devote time to graphite furnace work. He did report good success with development of a cold vapor atomic absorption method for mercury using the CETAC M6000-A mercury analyzer; the method should be available soon for collaborative study (2). Several interesting aspects of the method are (1) complete digestion of the sample is not required; (2) sensitivity (detectivity) is 1–2 orders of magnitude lower than that offered by existing food methods; (3) the ma-

trix modifier should work on a variety of dedicated instruments with similar detection capabilities; (4) a technique was developed to reduce losses of mercury at the low part-per-trillion concentration level.

Graphite Furnace Atomic Absorption Spectrometric Determination of Chromium in Foods

Study Director Nancy J. Miller-Ihli reported that work on this topic should be considered complete. She is considering pursuing peer-validation of a graphite furnace atomic absorption spectrometric method for low levels of chromium in foods.

Graphite Furnace Atomic Absorption Spectrometric Determination of Lead in Sugar and Sugar Products

Study Director Nancy J. Miller-Ihli reported that work on this topic should be considered complete.

Graphite Furnace Atomic Absorption Spectrometric Determination of Lead and Cadmium Released from Ceramicware

Study Director Susan C. Hight reported no further activities on this topic following AOAC approval of the collaborative study.

Lead in Calcium Supplements

Study Director Paul H. Siitonen reported no activity during the past year. He hopes to be able to commit personnel to trace element research in the near future and thus additional progress in this area may be possible.

Lead in Wines

Study Director Alan L. Reisig reports that for the collaborative study, (G-21) "Determination of Lead in Beverage Alcohol Using Graphite Furnace Atomic Absorption Spectrometry," additional statistical analysis was performed and resubmission of the method is contemplated.

Neutron Activation Analysis

Study Director William C. Cunningham indicated that this topic be discontinued, feeling that there is insufficient demand for neutron activation methods.

Metals in Foods by Atomic Absorption Spectrometry

Method Advisor Lars Jorhem reported no new activities following adoption of 2 methods: **999.10**, Lead, Cadmium, Zinc, Copper, and Iron in Foodstuffs, Atomic Absorption Spectrophotometry after Microwave Digestion and **999.11**, Determination of Metals in Foodstuffs, Atomic Absorption Spectrophotometry after Dry Ashing.

Recommendations

(1) *Atomic Absorption Spectrometry*: Study Director Milan Ihnat, Pacific Agri-Food Research Centre-Summerland,

Agriculture and Agri-Food Canada, Summerland, British Columbia V0H 1Z0, Canada, Tel: +1-250-494-6411, Fax: +1-250-494-0755, E-mail: ihnatm@agr.gc.ca. Submit to *J. AOAC Int.* a report "Flame Atomic Absorption Spectrometric Methodologies for Food Analysis—A Review," comprehensively summarizing the status of current flame atomic absorption spectrometric methods used by AOAC INTERNATIONAL and other agencies for major, minor, and trace elemental levels in foods and agricultural products. Complete development of a unified, comprehensive, multielement flame atomic absorption scheme of analysis of foods for a range of major, minor, and trace elements and submit for collaborative study approval and publication in *J. AOAC Int.* Complete a report for submission to *J. AOAC Int.* on the development and application of a highly reliable flame AAS method for multielement determinations in biological materials. Continue study.

(2) *Elements in Foods, Feeds, and Biological Materials by Inductively Coupled Plasma Atomic Emission Spectrometry*: Adopt new topic and appoint Study Directors.

(3) *Elements in Foods, Feeds, and Biological Materials by Inductively Coupled Plasma Mass Spectrometry*: Adopt new topic and appoint Study Directors.

(4) *Lead, Cadmium, Mercury in Foods by Graphite Furnace Atomic Absorption Spectrometry and Other Techniques*: Topic Advisor Robert W. Dabeka, Health Canada, Health Protection Branch, Food Research Division 2203D, Ottawa, Ontario K1A 0L2, Canada, Tel: +1-613-957-0951, Fax: +1-613-941-4775, E-mail: Bob_Dabeka@hc-sc.gc.ca. Bring under this heading and this Advisor the topics Graphite Furnace Atomic Absorption Spectrometry and Lead in Foods. Continue with research development into methods for lead in foods utilizing determinative techniques of inductively coupled plasma mass spectrometry and graphite furnace atomic absorption spectrometric techniques and development of preconcentration techniques as may be required. Incorporate into this topic and under this Advisor the topic Mercury in Foods. Continue development of the cold vapor AAS method for mercury. Change name of topic to reflect new activities. Continue study.

(5) *Graphite Furnace Atomic Absorption Spectrometric Determination of Chromium in Foods*: Study Director Nancy J. Miller-Ihli, U.S. Department of Agriculture, Beltsville Human Nutrition Research Center, Nutrient Composition Laboratory, Bldg 161, BARC-East, Beltsville, MD 20705, Tel: +1-301-504-8252, Fax: +1-301-504-8314, E-mail: miller-ihli@bhnrc.usda.gov. Complete the collaborative study or peer-validation on the graphite furnace atomic absorption method for the determination of chromium in foods and biological materials, based on the method published (3). Continue study.

(6) *Graphite Furnace Atomic Absorption Spectrometric Determination of Lead in Sugar and Sugar Products*: Study Director Nancy J. Miller-Ihli. Discontinue topic.

(7) *Graphite Furnace Atomic Absorption Spectrometric Determination of Lead and Cadmium Released from Ceramicware*: Study Director Susan C. Hight, U.S. Food and Drug Administration, Center for Food Safety and Applied Nu-

trition, Elemental Research Branch, HFS-338, 5100 Paint Branch Pkwy, College Park, MD 20740-3835, Tel: +1-301-436-1652, Fax: +1-301-436-2632, E-mail: susan.hight@cfsan.fda.gov. Continue study.

(8) *Lead in Calcium Supplements*: Study Director Paul H. Siitonen, U.S. Food and Drug Administration, National Center for Toxicological Research, Division of Chemistry, 3900 NCTR Dr, HFT-230, Jefferson, AR 72079-9502, Tel: +1-870-543-7656, Fax: +1-870-543-7686, E-mail: psiitonen@nctr.fda.gov. Complete evaluation of the precollaborative trial based on the proposed collaborative study method (4). Revise the collaborative study protocol to include the microwave dissolution procedure and prepare a protocol for collaborative study for approval by the General Referee, Committee Statistician, and Committee on Residues. Continue study.

(9) *Lead in Wines*: Study Director Alan L. Reisig, BATF Laboratory, 1401 Research Blvd, Rockville, MD 20850, Tel: +1-301-762-9800, Fax: +1-301-413-9463, E-mail: Alreisig@atfhq.atf.treas.gov. Complete revision of the collaborative study, "Lead in Beverage Alcohol, Graphite Furnace Atomic Absorption Spectrometric Method," following additional statistical analysis which were performed and resubmit modified method. Continue study.

(10) *Neutron Activation Analysis*: Study Director William C. Cunningham, U.S. Food and Drug Administration, Center for Food Safety and Applied Nutrition, Elemental Research Branch, mailing address: National Institute of Standards and Technology, Mailstop 8395, Gaithersburg, MD 20899-8395, Tel: +1-301-975-6271, Fax: +1-301-208-9297, E-mail: william.cunningham@nist.gov. Accept resignation of Study Director Cunningham with thanks for past activities on this topic. Methods based on neutron activation analysis may be looked upon as more specialized than most other methods due to the requirement, for typical applications, of a nuclear reactor as a source of neutrons. Instrumental neutron activation analysis (INAA) and neutron activation analysis with radiochemical separation (RNAA) are 2 common variants. Other subdivisions include thermal, epithermal, and prompt gamma versions of INAA, photon-induced activation analysis, and proton activation analysis. In addition, nonreactor sources can be used to provide excitation. The excellent multielement performance of activation-based methods makes it desirable to obtain at least generic versions of neutron activation methods for foods into official status. Continue topic; search for new Study Director.

(11) *Organometallics in Fish*: Continue Official First Action status of the Mercury (Methyl) in Seafood, Liquid Chromatographic-Atomic Absorption Spectrophotometric Method, **990.04**. Discontinue topic.

(12) *Metals in Foods by Atomic Absorption Spectrometry*: Method Advisor Lars Jorhem, National Food Administration, Box 622, S-751 26 Uppsala, Sweden, Tel: +011-46-18-17-55-00, Fax: +011-46 18 10 58 48, E-mail: lajo@slv.se. Continue monitoring any reports from users of the Official Methods **999.10** and **999.11**.

References

- (1) Ihnat, M. (2001) "Proposals for the Use of Reference Materials and for the Development of In-House Quality Control Materials for Food Analysis" in *Report of the Consultants Meeting on Proper Use of Reference and Control Materials*, IAEA, Vienna, Austria, (Ihnat) 1–31
- (2) Dabeka, R.W., Bradley, P., and McKenzie, A.D. (2002) *J. AOAC Int.* **85**, 1136–1143
- (3) Miller-Ihli, N.J., & Greene, F.E. (1992) *J. AOAC Int.* **75**, 354–359
- (4) Siitonen, P.H., & Thompson, H.C. (1998) *J. AOAC Int.* **81**, 1233–1239