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Influence of digestion methods on the determination of total Al in food samples by ICP-ES

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Summary. To determine total Al in a variety of food and total diet samples using ICP-ES, HF pre-treatment, prior to wet digestion ($HNO_3/HClO_4$) seems to be necessary. Compared with results obtained after HF pre-treatment, the determination of Al using pressure microwave digestion with HNO_3 or $HNO_3/HClO_4$ digestion recovered only between 25–50% Al for dried spinach and flour and 40–75% for total diet samples, respectively. In most cases the addition of 0.25 ml HF (40%) per gram dry mass resulted in maximum Al yield. The results are in acceptable agreement with those obtained by neutron activation analysis (NAA).

Introduction

There are some indications that – among other parameters – Al may be correlated to symptoms of neurological diseases, e.g., Alzheimer's disease [1, 2]. Consequently, factors that may possibly affect human health are studied, including Al contents of food. Thus the interest in reliable Al analyses of biological samples has significantly increased. Unfortunately the number of available and suitable reference materials is very limited, in particular when considering Al concentrations of less than 10 mg/kg [3, 4]. In order to improve the accuracy of Al results in this concentration range, special care has to be taken during sample preparation and measurement as Al is ubiquitous and may contaminate the sample [5–8]. In addition, some of the Al seems to be firmly bound even in biological materials – most probably associated with Si and may be withdrawn from analysis due to incomplete dissolution of Al containing constituents. Since these constituents are also not digested in the stomach, they most probably have no biological relevance for humans. However, their existence needs to be considered when comparing results obtained by NAA – giving information on the total Al content – and other methods, which require sample dissolution. The need of HF addition for complete dissolution has already been mentioned in determining other elements [9, 10]. Using ICP-ES the reliability of different digestion methods to determine trace elements was studied with regard to total Al content in daily diets and food related samples.

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Experimental

Three different dissolution methods were tested:

- $HNO_3/HClO_4$ digestion in a capped teflon beaker;
- $HNO_3/HClO_4$ digestion including pre-treatment using HF/HNO_3;
- HNO_3 digestion using microwave pressure bombs.

Reagents

Reagent grade HNO_3 was purified by sub-boiling distillation in a quartz still (Kürner). HF and $HClO_4$ were of suprapure grade (Merck). Water was passed through an ion exchanger (Aqua Lang) and distilled afterwards to eliminate resin particles. A 1000 mg/l single element standard solution of Al was used to prepare calibration solutions of 2.5 and 5 mg/l, respectively. To check possible interferences and instrument stability, mixed solutions containing known Al concentration (Spex company and NIST National Institute of Standards and Technology) as well as home made matrix matching solutions were used. All reagents and element standards for matrix elements were checked for Al content.

Measures to prevent contamination

Besides the fact that only suprapure or additionally distilled reagents were used, all the preparatory work was done in a clean room, mainly inside a laminar flow bench (class 100) equipped with exhaust system allowing work using acids (excluding: HF/HNO_3 evaporation step).

Materials used for sample preparation consisted of polyethylene or teflon which were treated with 20% HNO_3 for at least 3 days at room temperature, after the usual washing procedure (dish washer, no washing powder and rinsing 3 times with distilled H_2O). Subsequently they were rinsed with H_2O, stored under pure H_2O and, if necessary, dried before use.

Teflon digestion containers were additionally steamed with conc. HNO_3 for at least 4 h and subsequently stored under pure H_2O.

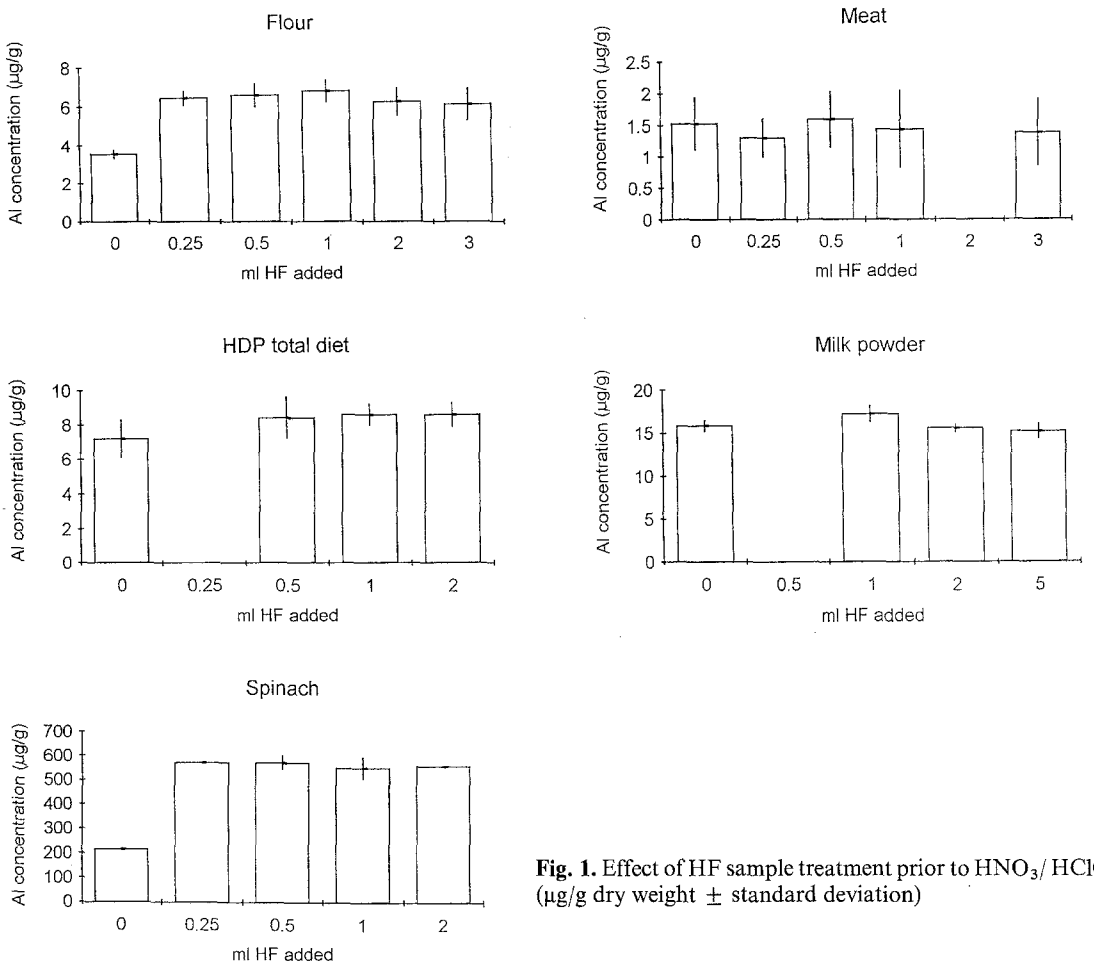

Fig. 1. Effect of HF sample treatment prior to HNO_3/ $HClO_4$ digestion on Al recovery (µg/g dry weight ± standard deviation)

Filter paper [Schleicher and Schuell (medium porosity)] was leached for 1 h using 20% HNO_3, rinsed with clean H_2O and used immediately.

The incoming air for the instrumental laboratory was treated using filters with a medium degree of separation (92%, EU4 DIN 24185).

Sample preparation

Procedure A: $HNO_3/HClO_4$ digestion. Approximately 1 g of sample was weighed into a screw-capped teflon beaker. 10 ml of HNO_3 (65%) and 3 ml of $HClO_4$ (70%) were added. The vessel was closed and after a reaction time of approximately 1 h placed into a drying oven inside a fume hood. The oven temperature was slowly increased to 105° C and the sample treated for 1 h. After cooling, the solution was diluted to 100 ml using distilled H_2O and filtered through filter paper.

Procedure B: $HNO_3/HClO_4$ digestion using HF/HNO_3 pretreatment. After weighing 1 g of sample into a teflon beaker, 5 ml HNO_3 and varying amounts of 40% HF (0.25 – 5 ml) were added and evaporated to dryness on a heating plate. (Note: initial stand by time of 1 h prior to heating reduces spilling due to vigorous reaction).

Then HNO_3 and $HClO_4$ were added and procedure A was followed.

Procedure C: pressure microwave digestion. 0.25 g of sample was weighed into a teflon beaker of a "Parr" ® type microwave bomb. 2.5 ml HNO_3 (65%) were added, the beaker capped and the bomb assembled and positioned in a household microwave oven equipped with a rotating plate. Power was turned to 150 W for 1 min and after approximately 30 min cooling time to 450 W for an additional minute. Pressure in the bomb was allowed to decrease by cooling for about 1 h. The sample was transferred into a 25 ml polyethylene volumetric flask and diluted to appropriate volume with distilled H_2O.

Blanks. For the "closed system" procedures A and C two blanks were made; for the "open system" procedure B, which is more susceptible to contamination, 3 blanks were prepared.

Measurements. ICP-ES measurement was performed using a Plasmakon 32 (Kontron). The line at 396.152 nm was chosen to determine Al and a "two sided" background correction was used to compensate for the Ca interference (−0.073 nm and +0.030 nm related to peak location).

A three-point calibration was performed using a blank and 2 Al standards (2.5 + 5 mg/l) in a 10% HNO_3 (vol./vol., prepared from 65% HNO_3) solution.

Samples were measured by collecting data for at least 3 consecutive (8 s each) integration periods. Matrix matching control solutions covering the expected Al concentration

Table 1. ICP-ES Results of total diet samples and reference materials. Concentrations given in mg/kg dry mass ± standard deviation. Comparison of digestion methods and NAA

Samples reference materials	Certified or information values*	$HNO_3/HClO_4$ digestion	Microwave pressure digestion	$HNO_3/HClO_4$ digestion with HF pre-treatment	Some literature values
Total diet 5		5.4 ± 0.9	5.2 ± 0.9	7.7 ± 1.1	11.0 [15], NAA
Total diet 611		19.3 ± 0.6	25.0 ± 1.1	35.9 ± 2.8	35.0 [15], NAA
Total diet 363		9.5 ± 0.8	10.9 ± 0.5	15.4 ± 1.4	15.0 [15], NAA
Total diet 635		13.0 ± 0.9	18.4 ± 0.9	22.9 ± 1.3	24.0 [15], NAA
Total diet IAEA H-9	9*	6.8 ± 0.4	7.1 ± 0.6	10.9 ± 1.4 (n = 6)	9.7 ± 0.7 [11] NAA 9.5 ± 2.0 [11]
Total diet 8431 NIST RM 8431	4*	5.2 ± 0.9	5.3 ± 0.5	6.7 ± 0.8 (n = 5)	3.9 ± 1.1 [12] NAA 6.4 ± 0.7 [12] NAA 4.7 ± 0.3 [12]
Citrus leaves SRM 1572	92.0 ± 15.0	34.0 ± 0.7		77.2 ± 2.4 (n = 4)	75 ± 2 [14, 16] NAA 76.5 ± 2.2 (n = 2) [13] 91.6 ± 9.9 [10] 78 ± 12 [14]
Orchard leaves SRM 1571		85.7 ± 2.8		359 ± 2 (n = 3)	323 ± 112 (n = 51) [13] 400 ± 60 (n = 19) [13] NAA
Whey powder IAEA 155	53 ± 15*			47.1 ± 1.4 (n = 6)	
Milk powder IAEA A-11	1.3 ± 0.6*	< 1		< 1 (n = 3)	

range of the samples were run regularly to check for optical instrument drifts.

Quality control. For quality control measurements IAEA (International Atomic Energy Agency) and NIST (National Institute of Standards and Technology) reference materials were included in the study. SLRS-1 riverine water standard (National Research Council of Canada) was used to check measurement accuracy at low concentration ranges.

Results and discussion

The use of high pressure microwave digestion compared to $HNO_3/HClO_4$ digestion showed only a slight increase of Al recovery (Table 1). Pre-treatment using HNO_3/HF prior to $HNO_3/HClO_4$ digestion results in a significant increase in the Al yield for spinach and flour amounting to a factor of 2–3. Samples like milk and meat, which are not so much exposed to ambient dust, showed no significant response to HF treatment (Fig. 1). For the total diet samples higher Al concentrations were found after HF pre-treatment. The amount of Al in total diet samples depends on their composition. The Al yield after HF treatment was 42%–76% higher compared with $HNO_3/HClO_4$ digestion only. The recovery increase of 42.6% for H-9 after HF treatment may explain the difference of results between two groups which were identified in the IAEA intercomparison run: one group of laboratories found on average 7.14 ± 0.49 mg/kg (n = 6), whereas the second group reported mean values of 10.69 ± 1.45 mg/kg (n = 5) [11]. Therefore Al in IAEA H-9 was not certified.

The effect of increasing amounts of HF on the yield of Al in flour, milk powder, spinach, meat and IAEA H-9 is demonstrated in Fig. 1. Nearly constant recoveries for Al were found after adding 0.25 ml – 1 ml HF (40%)/g of dried sample.

The reliability of ICP-ES results after HF pre-treatment is acceptable when compared with values obtained using NAA (neutron activation analysis) (Table 1).

Discussion of blank and quality control samples

Special care was taken during analysis to avoid Al cross-contamination. Although blank values decreased with increasing analytical experience they still were not very satisfying. Al results of 12 ± 2 ng/ml at a detection limit of 8 ± 3 ng/ml (in 10% HNO_3 solutions) indicated that improvements during sample preparation are necessary. Sanz-Medel et al. [7] recommended to place the ICP-ES system inside a laminar flow bench.

Working with pressure bombs and closed systems may decrease contamination problems. However, except for ambient air, HNO_3 remains the main source of increased blank values. Cleaning of reagents and materials using EDTA extraction may result in a lower Al content in the blank solution [8]. HF itself, even at high concentration did not contribute to the blank.

Results for SLRS-1 (21 ± 2 ng/ml; n = 4) agreed well with the certified Al value of 23.5 ± 1.2 ng/ml. This indicates that even at low Al concentrations and in a matrix containing higher levels of Ca (25 mg/kg) the double sided background setting compensates the interference caused by Ca at 396.847 nm.

The agreement of NAA Al results for IAEA H-9 with those of HF pre-treatment was acceptable. The average Al result for NIST total diet RM8431 using ICP-ES and HF pre-treatment was significantly higher compared to the information value of 4 mg/kg (Table 1). During characteriza-

tion of this reference material also higher results were reported, e.g. one NAA Al result of 6.4 ± 0.7 mg/kg [12]. However this result was identified as an outlier and eliminated prior to final evaluation. This value would be in good agreement with our findings.

This procedure can also be applied to other biological reference materials (Table 1). The agreement with literature and information or certified values is satisfying. Results obtained by NAA agree especially well. The high standard deviation of some results may indicate some analyticlal problems and (or) reflects difficulties in achieving agreement among different methods (e.g. during certification for citrus leaves NIST SRM 1572 and whey powder IAEA 155). However, it is promising that the values for citrus and orchard leaves obtained by a compilation study [13] agree well with our findings. But the range of results (99–824 mg/kg for Al) reported for orchard leaves in this compilation clearly pointed out the problems occurring during Al analysis.

Conclusion

Analysis of total Al without HF pre-treatment gives erroneous results for most food and total diet samples. Use of microwave techniques and high pressure does not improve the dissolution of some Al containing constituents. This effect is more significant for food items (increase of a factor 2–3), which possibly have been in contact with dust and ambient air, while milk and meat shows nearly no recovery increase when using HF.

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References

1. Crapper DR, Krishnan SS, Dalton AJ (1971) Science 180:511–513
2. Krishnan SS, et al (1988) Essential and toxic trace elements in human health and disease. Liss, New York, p 645
3. Cortes Toro E, Parr RM, Clements SA (1990) Biological and environmental reference materials for trace elements, Nuclides and Organic Microcontaminants. IAEA/RL 128 (Rev. 1)
4. NIST Standard Reference Materials Catalogue 1990–1991, Special Publication 260
5. Uehara N, Kanbayasi M, Hoshino H, Yotsuyanagi T (1989) Talanta 36:1031–1035
6. Jorham L, Sundstrom B, Astrand C, Heagglund G (1989) Z Lebensm Unters Forsch 188:39–44
7. Sanz-Medel A, Rodriquez Roza R, Gonzales Alonso R, Noval Vallina A, Connata J (1987) J Anal Atomic Spectrom 2:177–185
8. Nordahl K, Radziuk B, Thomassen Y, Weberg R (1990) Fresenius J Anal Chem 337:310–315
9. Wikoff LR, Moraghan JT (1986) J Sci Food Agric 37:839–844
10. Zunk B (1990) Anal Chim Acta 236:337–343
11. Parr RM: Report on the intercomparison run H-9 trace elements in total diet. (IAEA unpublished data)
12. Miller-Jhli N, Wolf WR (1986) Anal Chem 58:3225–3230
13. Gladney ES, O'Mailey BT, Roelandts J, Gills TE (1987) Compilation of elemental concentration data from NBS clinical, biological, geological and environmental standard reference materials. NBS 266–111
14. Landsberger S, Arendt AM (1989) J Radioanal Nucl Chem 137:443–454
15. Parr RM, et al: unpublished NAA-results from an IAEA Coordinated research programme on human daily dietary intakes of nutritionally important trace elements
16. Glascock MD, Tian WZ, Ehmann WD (1985) J Radioanal Nucl Chem (Articles) 92:379