

## INCOMPLETE RELEASE OF FLUORIDE BY ULTRASOUND FROM PLANT SAMPLES

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**SUMMARY:** Cold ultrasonic treatment at 40 kHz of finely ground plant samples under the best conditions examined (6 M HClO<sub>4</sub>, 360 min) released a maximum of only 37% of the fluoride present according to fluoride ion selective electrode analysis. An optimized Teflon bomb digestion method (65% HNO<sub>3</sub> for 6 hr at 120 °C) gave quantitative recovery of fluoride in various standard plant samples as well as in the residues from the sonication treatment. Despite its convenience, cold ultrasound is not a satisfactory method for treatment of plant samples for release of fluoride for analysis.

Keywords: Fluoride determination; Fluoride in plants; Ion selective electrode, Teflon bomb digestion; Ultrasound treatment.

### INTRODUCTION

Plant vegetation is more sensitive to fluoride than to most other air pollutants. As a result, the fluoride content of plants is extensively used for diagnosis of injury and as an air quality standard.<sup>1-4</sup>

Accurate determination of fluoride in plants is critically dependent on sample preparation due to the different forms in which fluoride is present. The most used pretreatment procedures are open ashing, alkali fusion, oxygen combustion, and acid digestion; these procedures are usually followed by separation or concentration steps such as leaching, distillation, diffusion, pyrolysis, solvent extraction, ion-exchange, and precipitation.<sup>5-9</sup> The concentration of F<sup>-</sup> in the final solution is usually determined by titrimetric, spectrophotometric, potentiometric, or ion chromatographic techniques,<sup>10-14</sup> which are sometimes subject to interference. The fluoride ion selective electrode is highly specific for F<sup>-</sup> in water, but the operating conditions require control of pH and ionic strength, along with the presence of chelating agents to prevent interference from polyvalent cations.<sup>15-17</sup>

Cold ultrasound treatment is a clean technique that is used to increase rates of chemical reactions and can lead to leaching of elements from different kinds of samples. It is often one of the preferred techniques for sample preparation due to its selectivity, formation of a matrix-free solution, relatively short extraction time, lower consumption of chemical reagents, negligible amounts of by-products, and environmental cleanliness.

This work focused on studying experimental conditions (exposure time, kind and molarities of reagents) of the ultrasonic technique for releasing fluoride from plant samples and its determination using the fluoride ion selective electrode. Results are compared with Teflon bomb digestion using standard reference materials.

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## MATERIALS AND METHODS

*Apparatus and reagents:* Electrode measurements were carried out using a Metrohm 692-pH/ion meter (fluoride electrode and AgCl reference electrode), an ultrasonic unit (Transsonic T 1060/H, Elma, Germany), Teflon bombs (30 mL capacity, Parr Instrument Co., Moline, Illinois, USA), analytical-grade chemical reagents (Merck GR), and double distilled water.

*Sample preparation:* Chickpea grain samples were collected from the southern part of Syria, and wheat-plant samples were collected from an area surrounding a phosphate fertilizer plant in central Syria. The wheat-plant samples were washed with distilled water, dried in an oven at 75 °C for 24 hr, milled, then sieved through 100-200 mesh aperture sieves, and shaken overnight. The chickpea grain samples were ground using an agate mortar, sieved, and also shaken overnight. Three plant reference samples (Beech-leaves RM-100, Orchard-leaves from IAEA, and Sample 638 (IPE) from the Netherlands) were used to assess the ultrasonic and Teflon bomb methods for fluoride content.

*High-pressure Teflon bomb digestion:* Three sub-samples (0.1 g) of each certified reference sample and eighteen chickpea sub-samples were each put into the 30 mL Teflon bombs, which were divided into six groups of three bombs. Each sample from the first group was spiked with 5 µg of fluoride dispensed by an electrical micropipette from a standard NaF solution (10 or 100 µg F<sup>-</sup>/mL), while those of the second group were spiked with 10 µg, the third group with 15 µg, the fourth group with 20 µg, and the fifth group with 25 µg each, while those of sixth group were left un-spiked. One mL of nitric acid (65%) was added to each bomb vessel; the vessels were tightly closed and heated in an oven at 120 °C for 6 hr. After cooling, the pH was adjusted to 5.5 using 10 M KOH solution, and 1.25 mL of 0.8 M trisodium citrate dehydrate (C<sub>6</sub>H<sub>5</sub>Na<sub>3</sub>O<sub>7</sub>·2H<sub>2</sub>O) was added and the solution was diluted to 25 mL with distilled water for fluoride determination by the fluoride ion selective electrode, which was found to be essentially linear on a log[C] plot between 0.01 and 100 µmg F<sup>-</sup>/mL and was verified using certified plant samples and spiked chickpea samples.

Ten sub-samples (0.1 g) of wheat-plant samples were directly digested in 30 mL Teflon bombs under the same conditions, and five groups with three sub-samples each were digested after each sample from each group were spiked with one of the following amounts of fluoride dispensed as above from a standard NaF solution: 25, 50, 75, 100 and 125 µg. The fluoride ion concentrations in the resulting 25 solutions were then determined. These samples, labeled as sample (A), were used to compare with the capability of the ultrasonic technique for fluoride recovery.

*Cold ultrasonic extraction:* The positions of maximum wave pulses were determined using the aluminum foil mapping technique.<sup>18</sup> Fifteen sub-samples (0.5 g) from sample (A) and fifteen sub-samples (0.5 g) from the chickpea sample were each put into a 10 mL stoppered polyethylene vial, and each series was divided into five groups of three vials each. One 3 mL portion of 7 M HNO<sub>3</sub>, 6 M HCl, 6 M HClO<sub>4</sub>, 7 M HNO<sub>3</sub> + 6 M HCl, and 7 M HNO<sub>3</sub> + H<sub>2</sub>O<sub>2</sub> was added to the vials

of each group which were exposed to 40 kHz ultrasonic waves for 15 min. The same procedure was repeated on an additional four groups of sub-samples for exposure to ultrasonication for 30, 45, 60, and 360 min.

As a further experiment, 0.5 g samples from sample (A) and five sub-samples (also 0.5 g) from the chickpea sample were each put into 10 mL polyethylene vials, and 3 mL of 6 M HClO<sub>4</sub> was added to each vial. The vials were exposed to ultrasonic waves for 360 min; the samples were filtered, and each residue was transferred to a 30 mL Teflon bomb, and 1 mL of 65% nitric acid was added to each. The bombs were heated in an oven at 120C for 6 hr. Three sub-samples (0.5 g) of each of the three certified reference samples were each put in a 10 mL polyethylene vial, and 3 mL of 6 M HClO<sub>4</sub> was added to each vial. The vials were exposed to ultrasonic waves for 360 min, and the fluoride ion concentration was determined in the resulting solutions as above in the Teflon bomb section.

### RESULTS AND DISCUSSION

The Teflon bomb method is considered a reliable procedure in which the recovery of fluoride is quantitative. Tables 1 and 2 confirm its consistency and reproducibility; the standard samples gave results that are within  $\pm 3\%$  of the certified values.

**Table 1.** Means of three replicates of Teflon bomb digestion (0.1g, 1 mL HNO<sub>3</sub>, heating at 120C for 6 hr) and ultrasonic extraction (0.5 g, 3 mL 6 M HClO<sub>4</sub>, 360 min exposure time) of plant reference samples for fluoride determination ( $\mu\text{g/g}$ )

Reference sample	Certified value $\mu\text{g/g}$	Teflon bomb	Ultrasonic extraction
Beech leaves	20.9	21.7 $\pm$ 0.5	2.6 $\pm$ 0.1
Orchard leaves	4.00	3.9 $\pm$ 0.1	0.55 $\pm$ 0.03
638 (IPE)	5.36	5.2 $\pm$ 0.1	0.68 $\pm$ 0.05

These findings also apply to the internal wheat plant and chickpea grain samples that were studied extensively by direct digestion and digestion after being spiked with different amounts of fluoride.

**Table 2.** Means of three replicates of Teflon bomb digestion of wheat Plant sample A and chickpea sample with and without fluoride spiking ( $\mu\text{g/g}$ )

Sample A	260 $\pm$ 7	Chickpea	38.0 $\pm$ 0.6
Sample A+25 $\mu\text{g F}^-$	276 $\pm$ 8	Chickpea+5 $\mu\text{g F}^-$	42.6 $\pm$ 0.7
Sample A+ 50 $\mu\text{g F}^-$	311 $\pm$ 10	Chickpea+10 $\mu\text{g F}^-$	47.7 $\pm$ 0.6
Sample A+75 $\mu\text{g F}^-$	335 $\pm$ 9	Chickpea+15 $\mu\text{g F}^-$	53.5 $\pm$ 0.9
Sample A+100 $\mu\text{g F}^-$	362 $\pm$ 10	Chickpea+20 $\mu\text{g F}^-$	57.2 $\pm$ 0.8
Sample A+125 $\mu\text{g F}^-$	386 $\pm$ 8	Chickpea+25 $\mu\text{g F}^-$	63.0 $\pm$ 1.0

Another proof of the consistency and reproducibility of the Teflon bomb digestion is shown in Table 3, where the remaining residuals from ultrasonic extraction were digested and always completed the recovery of fluoride to 100%. However, this consistency and reproducibility were only achieved with the use of 65% nitric acid at 120 °C for 6 hr.

**Table 3.** Means of five replicates of ultrasonic extraction (0.5 g, 3 mL 6 M HClO<sub>4</sub>, 360 min) and Teflon bomb digestion (1 mL HNO<sub>3</sub> at 120 °C for 6 hr) of the residue remaining after ultrasonic extraction of fluoride from wheat sample A and chickpea sample

	Sample A	Chickpea
Percentage of F <sup>-</sup> extracted by ultrasound	37±4%	32±4%
Percentage of F <sup>-</sup> after ultrasound extraction	63±2%	67±2%
Total percentage	100±3%	100±2%

A wide range of experimental conditions were explored to optimize ultrasonic extraction of fluoride from standard plant samples, but the results were always much lower than the certified values. Even under the best conditions (6 M HClO<sub>4</sub> for 360 min), only 37% of the total fluoride was extracted compared to 21% extracted after 15 min. With extraction times ranging from 15 to 360 min, various concentrations of hydrochloric acid or nitric acid (the latter with and without 30% hydrogen peroxide present) gave a maximum of 33% extraction.

As shown in Table 3, the Teflon bomb conditions applied to the residues from the same samples in the ultrasonic extraction gave 100% recovery of the fluoride present. The accuracy of the Teflon bomb method was evaluated using standard plant reference materials, but due to the lack of a grain reference material, a standard addition method was used for the chickpea sample as shown in Table 2. In these experiments, the maximum percentage error was 2%, and the precision was 0.0073 g/mL in the ion specific electrode measurements.

#### ACKNOWLEDGMENTS

The author wishes to thank Prof I Othman, Director General of the Atomic Energy Commission of Syria, and Prof G Zayzafoon, Head of the Chemistry Department, for their support and encouragement. Also, I extend my thanks to Mrs Z Hariri who performed the ion selective electrode measurements.

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