INDUSTRIAL FLUORIDE POLLUTION OF VEGETABLES IN HUBEI PROVINCE, CHINA

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SUMMARY: Fluoride concentrations in vegetables grown in areas 3 km and 45 km away from the fluoride polluting Wuhan Iron and Steel Factory of Hubei province, China, were determined by ultra-sensitive single-sweep polarography. Vegetables from as close as 3 km to the factory have about double the fluoride content as those grown 45 km distant. Cleaning the polluted vegetables with water reduced the fluoride content to nearly the same level as in vegetables grown 45 km away from the factory, thereby indicating that most of the polluting fluoride can be removed by appropriate washing.

Keywords: Airborne fluoride; Fluoride analysis; Fluoride in vegetables; Hubei Province, China; Industrial fluoride pollution; Single-sweep polarography; Vegetables in China; Wuhan Iron and Steel Factory.

INTRODUCTION

In China, fluoride air pollution comes mainly from steel factories, ceramics works, and coal burning. For example, in 1999 the total quantity of fluoride released into the atmosphere from industrial production in China was estimated at 2 million tons, of which the amount from iron and steel works was at most about 30%.1 Vegetables exposed to airborne fluoride absorb it in their laminae,2,3 and people who consume these crops tend to ingest excessive amounts of fluoride. Therefore, the determination of fluoride in vegetables is of great importance.

Various methods for the determination of fluoride in food have been reported.4-7 However, some of them require expensive instrumentation, while others lack good sensitivity. For the work presented here we used a sensitive polarographic method involving a Pr(III)-ALC-F−-acetone system4 to determine the fluoride content of vegetables.

MATERIALS AND METHODS

Apparatus: A JP-2 Oscillographic Polarograph (Chengdu Instruments, China) and a three-electrode system with a dropping mercury working electrode were used. The reference and counter electrodes were saturated calomel and platinum electrodes.

Reagents: A standard fluoride solution (0.0100 mol/L) was prepared by dissolving 0.1050 g of reagent-grade sodium fluoride in 250 mL of distilled water and stored in a polyethylene bottle. This solution was then diluted to various lower concentrations as needed. Alizarin complexone (ALC) (1.0×10−3 mol/L) was prepared by dissolving 0.0964 g of ALC in 2 M sodium hydroxide, the solution was neutralized with 2 M nitric acid to pH ca. 4.9, and then diluted to 250 mL with distilled water. A standard Pr(III) solution (5.0×10−4 mol/L) was prepared by...

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dissolving 0.0413 g of Pr₂O₃ in dilute nitric acid and adjusted to pH 4.9. Aqueous hexamethylenetetramine (1.0 mol/L) was prepared as in our earlier report.⁴

**Analytical method:** Reagents were placed in a 10-mL volumetric flask as follows: 1.00 mL of 1.0 mol/L (pH, 4.9) hexamethylenetetramine solution, 0.20 mL of 1.0×10⁻³ mol/L ALC solution, 1.20 mL of 5.0×10⁻⁴ mol/L Pr(III) solution, a known amount of F⁻ standard solution, and 0.60 mL of acetone. The resulting solution was allowed to stand for 20 min and then diluted to 10 mL with distilled water. The derivative polarogram was recorded from −0.30 V to −0.80 V (vs. SCE) and the wave height measured at −0.65 V. The wave height was linear with the F⁻ concentration in the range of 1×10⁻⁷–2×10⁻⁶ mol/L with a correlation coefficient of 0.9997. The presence of acetone improved the stability of the Pr(III)-ALC-F⁻ complex, resulting in increased sensitivity, a lower detection limit of 5×10⁻⁸ mol/L, and less extraneous interference.

**Sample preparation and F⁻ determination:** During conditions of no wind, vegetables were randomly selected from a farm 3 km south of the Wuhan Iron and Steel Factory, Hubei province. The same kinds of vegetables grown in a region 45 km away from the factory were also selected. The samples were washed, dried, cut, and well mixed. A 5-g sample (fresh weight) was placed in a 30-mL porcelain crucible, and then 5.0 mL of magnesium nitrate solution (100 g/L) and 0.50 mL of sodium hydroxide solution (100 g/L) were added to the crucible. After evaporation of the contents on a water bath, the crucible was heated until fuming ceased and then transferred to a muffle furnace for incineration at 600ºC for 6 hr. After cooling, 10 mL of water and several drops of concentrated sulfuric acid were added into the crucible to neutralize the solution. The solution was transferred into a 500-mL distilling flask and 60 mL of concentrated sulfuric acid and several fluoride-free glass pearls were added before distillation. The distillate was collected in a 50-mL beaker containing 5 mL of 2% sodium hydroxide solution and one drop of phenolphthalein. When the distilling temperature reached 190ºC, the distillate was neutralized with 6 M hydrochloric acid.⁸ The solution was then transferred into a 100-mL volumetric flask and diluted to the mark with distilled water. For the fluoride analysis, the solution was used as described above in the analytical method. A 5-g batch of each vegetable was used to prepare 100 mL sample solution, and a 0.20 mL of sample solution was transferred to a 10-mL volumetric flask for the polarographic analysis, and the F⁻ content per g of sample was calculated. Results are summarized in Tables 1 and 2. For example, in Table 1: data for 12.54 µg F⁻/g = (0.01254 µg/mL×10 mL )/(5 g×0.20 mL )/100 mL.

In order to evaluate the validity of the procedure, 0.095 µg fluoride (from a solution of NaF) was added to 0.20 mL of analysis sample aliquot diluted to 10 mL to perform recovery analyses. The recovery values ranged from 96% to 106%.

**RESULTS AND DISCUSSION**

Fluoride concentrations found in vegetables grown in the polluted area 3 km from the Wuhan Iron and Steel Factory are shown in Table 1, and concentrations in the same vegetables grown 45 km away from the Wuhan Iron and Steel Factory are shown in Table 2.
As shown in Table 3, after the vegetables grown in the polluted area were cleaned with deionized water, the fluoride concentrations were greatly reduced, in three cases essentially to those in Table 2.

As seen in Table 1, the order of decreasing fluoride concentration among the vegetables grown in the area 45 km away from the Wuhan Iron and Steel Factory was: cauliflower > celery > hong cai-tai > Chinese cabbage, whereas in the more polluted area 3 km from the Wuhan Iron and Steel Factory it was: cauliflower > celery > Chinese cabbage > hong cai-tai. These results suggest that a large part of the fluoride in the vegetables is derived chiefly from their laminae absorbing and accumulating fluoride from the air. Among the above-mentioned vegetables, the exposed laminae area of cauliflower is the largest, and therefore cauliflower is more prone to absorbing fluoride. On the other hand, Chinese cabbage and hong cai-tai appear to absorb less fluoride in the polluted region. Moreover, as seen in Table 3, fluoride in the vegetables grown in the polluted area will be partially
eluted by soaking in clean water for 15 min, leading to about 50% reduction in $F^-$ concentration. It is suggested, therefore, that the polluted vegetables be carefully washed before cooking.

Table 3 also shows that even after washing, the vegetables have fluoride concentrations that still exceed the permitted value of 1 µg/g prescribed in the Chinese Food and Sanitation Standard. This indicates that the source of the fluoride pollution is probably from the soil and water, besides air. In order to prevent the vegetables in the suburbs from being polluted, any kind of fluoride emissions should be severely restricted. Furthermore, factors such as land layout and management should be taken into account so that vegetables are planted as far away from polluted regions as possible.

REFERENCES