

Rapid Determination of Fluorine in Solid Samples*

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A rapid method for the determination of fluorine in various matrices of geochemical and environmental interest is described. After fusion with NaOH, the sample is dissolved by means of tiron (= pyrocatechol-3,5-disulfonic acid, disodium salt), which acts both as buffer substance and as superior masking agent for cations exhibiting strong complexes with fluoride, e.g. Al, Fe, Ti etc. The final determination is done by means of the fluoride sensitive electrode without further separation.

The applicability of the method has been checked for various silicates, bauxite, phosphates, soils, coal and plant material. A detection limit of 10 $\mu\text{g/g}$ can be achieved, which is sufficient in many cases. The overall precision is better than $\pm 10\%$.

(Keywords: Ion selective electrode; Minerals; Plant material)

Eine schnelle Bestimmungsmethode für Fluor in festen Proben

Es wird eine schnelle Methode zur Bestimmung von Fluor in verschiedenen geochemischen und umweltrelevanten Matrices beschrieben. Nach Schmelzen mit NaOH wird die Probe mittels Tiron (= Brenzkatechin-3,5-disulfonsäure, Dinatriumsalz) gelöst, welches sowohl als Puffersubstanz als auch als überlegener Komplexbildner für Kationen wirkt, die starke Komplexe mit Fluorid bilden, wie z. B. Al, Fe, Ti etc. Die Endbestimmung erfolgt ohne weitere Trennung mit der fluoridsensitiven Elektrode.

Die Anwendbarkeit der Methode wurde bei verschiedenen Silikaten, Bauxit, Phosphaten, Böden, Kohle und Pflanzenmaterial überprüft. Eine Nachweisgrenze von 10 $\mu\text{g/g}$ kann leicht erreicht werden, was in den meisten Fällen ausreicht. Die insgesamt erzielte Genauigkeit ist besser als $\pm 10\%$.

Introduction

Increasing demands for rapid and correct methods for the determination of fluorine in both environmental and industrial samples increase the need of fast and reliable methods [1]. Concerning the analysis of solids, there is the question, how to get an appropriate solution of the

* Dedicated to Prof. Dr. K. L. Komarek on occasion of his 60th birthday.

analyte without any losses, and secondly, how to liberate the fluoride from its complexes, either by masking or by separation. Separation and enrichment of fluoride can be achieved by steam distillation from a sample treated with HClO_4 , with subsequent absorption of the steam in $\text{Al}(\text{NO}_3)_3$ -solution [2, 3]. Thus, the fluorine from samples up to 1 g can be collected in a final volume of 20 ml.

There are, however, some severe disadvantages of distillation methods. The output is low, only 3-4 determinations can be run a day. Samples insoluble in perchloric acid cannot be submitted to the distillation directly, but have to be treated with alkaline fluxes at first. Organic matrices have to be ashed prior to distillation. Last, but not least, the selectivity of the fluoride sensitive electrode, which is the most usual analytical tool for the determination of fluorine today, is much higher than the selectivity of the older spectrophotometric methods. So the need for exact separation methods dwindles away.

Because attack with acids leads to volatilization of HF, only alkaline fluxes can be used for decomposition. Fusion with NaOH is superior to NaKCO_3 , because it is done in a shorter time and at lower temperatures. At 450° it readily dissolves silicates, bauxite, TiO_2 and phosphates [4-10, 14]. In the presence of air the melt is oxidizing and destroys organic substances [13].

Use of Tiron as Complexing Agent for Dissolution

To avoid filtration and possible adsorption of traces upon precipitates [10, 11], it is preferable to use complexing agents for the dissolution of the flux as a whole. Strong acids would lead to vigorous evolution of CO_2 and also possible loss of HF or precipitation of silicic acid. Dissolution in citric acid also often requires filtration [5, 8, 10]. Ammoniumsulfosalicylate easily dissolves samples rich in Al and Fe, but the high *pH* of the reagent solution lowers the detection limit appreciably [9, 12]. Some authors add *EDTA* or *CDTA* to complex Mg and Ca, if present at higher levels [6, 9, 12].

In this work the reagent "tiron" (pyrocatechol-3,5-disulphonic acid, disodium salt) is introduced as a universal complexing and buffering agent. It reacts with Al, Fe, Ti, Be, Ca, and also with Si and B [15], so that any alkaline flux is dissolved easily by an excess of the reagent. After complete dissolution of the cooled flux in a solution of tiron, an aliquot of the sample is brought to *pH* 6.3-7.0 by addition of HCl, and the F-sensitive electrode is inserted. If there is too much acidification, the red iron-complex turns to blueish-green, so that a visual control is possible. In addition, tiron buffers both *pH* and ionic strength of the solution, thus no further reagent needs to be added [15].

Experimental

Reagents and Apparatus: Orion fluoride sensitive electrode 96-09-00. Orion Ionalyzer (mV-meter with logarithmic scale), or mV-meter with high internal resistance. Tiron = pyrocatechol-3,5-disulphonic acid, disodium salt, p.a., Loba-Chemie Nr. 14420 (Austria). Merck Neutralit, *pH*-sensitive paper (*pH* 5.5–9.0). HCl, NaOH p.a.; Pt-crucibles, muffle furnace, magnetic stirrer.

Procedure: 100 mg sample are weighed in a Ni- or Pt-crucible, 5 pellets of NaOH (about 1 g) are added and dissolved in some ml of distilled water. After mixing, the crucible is put into a muffle furnace and gradually heated to evaporate the water. (If this is done too fast, the NaOH solution climbs up the wall of the crucible.) Finally heating at 400°/20 min is sufficient in many cases, at higher temperatures the Pt is attacked to some extent. After cooling, the contents of the crucible is dissolved in some water with the aid 2 g tiron, transferred into a plastic volumetric flask (in which the tiron has been weighed) and brought to 50 ml with water.

For concentration measurement, an aliquot of 10 ml sample solution is pipetted into a plastic beaker, neutralized with 300 μ l HCl conc. and brought to *pH* 6–7 by addition of a few microlitres of HCl or NH₃ (diluted 1 : 1). While the sample is stirred with constant speed, the potential of the F-sensitive electrode is taken after it has reached a constant value. Calibration is done by subsequent addition of 10 or 20 μ l of 100 μ g/ml F-standard to a tiron blank solution, identical in tiron, NaCl concentration and *pH*. The calibration is repeated after every five samples. Between the measurements, the electrode is kept in pure water, till the potential of the reagent blind is observed.

Results and Discussion

The final determination of fluorine by means of the ion-selective electrode has found general acceptance, because it is fast and covers 5 orders of magnitude. Prior to determination, the sample has to yield free fluoride ions in the final solution. After fluxing with NaOH solution, an only double molar excess of tiron is sufficient to liberate the fluorine from its complexing cations, within the range *pH* 6–7. Sometimes the Pt-crucibles get brownish spots, which can be cleaned by melts of K₂S₂O₅ or LiBO₂. In case of coal, plant and wood samples, final heating to 550 °C for about an hour is needed to achieve complete oxidation. For coals, it is advantageous to moisten the sample with methanol/water [14].

If standards and samples are prepared in presence of the same amounts of reagents, there can be direct reading from a calibration curve, and no standard addition is needed.

Table 1 shows the maximum amounts of tolerable cations in the final solution and thus reveals the huge masking abilities of tiron.

Table 2 shows a list of samples which have been analyzed by the proposed method.

The applicability of the method has been checked for various silicates, bauxite, phosphates, soils, coal and plant material. A detection limit of

Table 1. Tolerable amounts of accompanying ions (calculated as percentage in the solid sample, when 100 mg are brought to a final volume of 50 ml)

	Acetate/CDTA pH 5.5 [%]	1 MK-Citrate pH 5.2 [6] [%]	0.2 M-Sulfosal. pH 8.5 [9] [%]	0.1 M-Tiron pH 6.5 [15] [%]
Ca	> 60	100	35	100
Al	0.1	1.5	3.3	25
Ti	1.25	4.5	0.5	25
Fe	1.9	70	2.0	25
La	—	5.0	5.0	> 5

Table 2. Analyzed samples

	Found [%]	Certified [%]
CCRMP syenite rock SY-2	0.53	0.51
CCRMP syenite rock SY-3	0.70	0.66
USGS GSP-1	0.38	0.37
ZGI GnA	3.14	3.36
stream sediment GSD-2	0.21	0.20
GSD-3	0.034	0.03
GSD-4	0.085	0.07
GSD-8	0.022	0.02
NBS bauxite 69 b	0.26	—
NBS phosphate rock 120 b	3.80	3.84
CCRMP soil SO-3	0.050	—
NBS coal 1 632 a	0.14	—
NBS coal 1 635	0.037	—

Round robin of the Austrian Research Centre Seibersdorf 1986:

Red clover Found: 5.8 $\mu\text{g/g}$ Range*: 2.5– 6.8
 Pine needles 30 $\mu\text{g/g}$ 24.5–33

* Scatter of values from all participants.

10 $\mu\text{g/g}$ can be achieved, which is sufficient in many cases. The overall precision is better than $\pm 10\%$. For measurements below 20 $\mu\text{g/g}$ in the solid sample, the calibration $\log |F|/\text{mV}$ is not linear any more, and a close fitting of calibration and standards is necessary. In this case, calibration has to be done with a more diluted standard solution.

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