

**The analysis of fluoride in tropical soils by selective ion electrode methods and its possible application to the search for sub-outcropping tin deposits in Peninsular Malaysia**

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**INTRODUCTION**

During recent years the development of analytical methods in which selective ion electrodes play a key role has permitted a number of elements (fluorine, sulphur, chlorine, etc.), of considerable interest to the applied geochemist, to be determined fairly simply and rapidly, over considerable concentration ranges. This prompted the writers to consider the possibility of using fluorine as a path-finder element during the search for primary, sub-outcropping tin deposits in Peninsular Malaysia. The results of the initial study form the substance of this note.

**DETAILS OF THE STUDY**

Two requirements were demanded of this initial study. The first was to investigate, in the laboratory, certain published procedures for the determination of cold-extractable and total fluorine, as fluoride, in geological samples, and to modify, if necessary, the best of these in order to obtain optimum results when local soil is the subject of analysis. The second was to establish the total and cold-extractable fluoride distribution patterns in the soil of a chosen stanniferous area and to determine if the establishment and analysis of such patterns would facilitate the search for sub-outcropping tin deposits there, and possibly in similar areas elsewhere in the country.

To some considerable extent the two objects were intertwined as the soils used in the study as a whole were those obtained from Tekka Hill in Perak, which is known to contain primary tin deposits. The soils were collected by one of us (GHT) from the B horizon, at points 50 feet apart, and along 3 traverses (Fig. 2), and for analysis the minus-80-mesh (B.S.S.) fraction of the oven-dried samples was used. Previous to the work under review GHT had analysed this fraction of each of the samples for tin and arsenic. However, during the initial laboratory work aimed at establishing the best analytical procedures for fluoride, International Rock Standards (see Table 1) were used as the yard-stick, and these were repeatedly analyzed.

**THE ANALYTICAL ASPECT**

**Instrumentation**

For the instrumental stages of the analysis a fluoride-sensitive electrode (Orion Research Model 94-09A) and a reference electrode (Orion Research Model 90-01-00) were used in conjunction with a direct-reading, expanded scale, millivoltmeter (either Orion

Research Model 801, or 801A). The fluoride sensitivity of the electrode depends on the potential difference between the faces of a  $\text{LaF}_3$  single crystal, which is embedded in the end of the electrode (Fig. 1). The outer side of the crystal is in contact with the sample solution whilst the inner side is bathed by the internal electrolyte consisting of a mixture of 0.1M NaF and 0.1M KCl.

Space does not permit discussion of the theory upon which this instrumental method is based. However, it can be found in the analytical papers referred to below.

Table 1

A comparison between the total fluoride content of certain International Standard rocks as recorded in the literature with that obtained by the writer using the modified method by Kesler et al (1973).

Sample	Literature values (ppm)	The writers' results			
		mean value (ppm)	No. of replicates	Standard deviation	Relative Standard deviation %
(i) USGS-GSP-1 Granodiorite	3900, 3800 4000, 3700	3907	6	481	12.3
(ii) CRPG-GA Granite	440, 487 500	588	8	88	14.9
(iii) CRPG-GH Granite	3000, 3100 3600, 4550	3624	5	258	7.1
(iv) CRPG-BR Basalt	990, 1100	964	5	187	19.4

- (i) Flanagan, F.J. (1969). US Geological Survey Standards-II. First compilation of data for the new U.S.G.S. rocks. *Geochem. et Cosmochimica Acta* Vol. 33, pp. 81-120.
- (ii)-(iv) Roubault, M., de La Rouche, H. and Govindaraju, K. (1968). Report (1966-1968) on geochemical standards: Granites GR, GA, GH; Basalt BR; ferrous Biotite Mica-Fe; Phlogopite Mica-Mg. *Sciences de la Terra*, Tome XIII, no. 4 pp. 379-404.

#### ANALYTICAL PROCEDURES

##### Cold-extractable fluoride

The method for determining cold-extractable fluoride, which was designed by Pluger and Friedrich (1972) was tested and found to be satisfactory. This involved treatment, in

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a beaker, of 0.5 g of the minus-80-mesh (B.S.S.) soil fraction with 25 ml of cold 0.01N HCl. During the attack of 30 minutes duration, the content of the beaker was stirred with a magnetic stirrer. The solution was then diluted with citric acid/di-sodium hydrogen phosphate buffer, at pH 6, and the electrode potential of the solution was compared with those of similarly prepared standards. From the readings the 0.01N HCl-extractable fluoride content was determined. This method allows fluoride to be determined over the range 1.0 to 5,000 p.p.m., and 70–80 complete analyses can be made per 8-hour, man-day.

### TOTAL-FLUORIDE

Initially, in an endeavour to determine the total fluoride content of the soils under examination, the total fluoride method of Pluger and Friedrich (1972) was employed, but this was abandoned as replicate analysis of International Standard rocks suggested that only c. 60–70 per cent of the total fluoride present was extracted. So, the writers' attention was turned to the method of Kesler, van Loon and Bateson (1973) and this, after certain minor modifications, provided results, when certain International Standards were analyzed by the method, that were sufficiently close to the published values to be acceptable. (See Table 1.)

Briefly the slightly modified analytical procedure is as follows:—

- i. Place 0.1 g of the sample in a nickel crucible then add 10 pellets of Analar NaOH.
- ii. Fuse for 2½ hours in a furnace at  $620^{\circ}\pm 10^{\circ}\text{C}$ .
- iii. Remove crucible from furnace. Cool: then half-fill it with distilled water, and allow it to stand for 10 minutes.
- iv. Transfer contents to a beaker and stir to disperse the gelatinous precipitate. Then add conc.  $\text{HNO}_3$ , with stirring, until the precipitate just dissolves.
- v. Dissolve 25 g ammonium citrate in the solution and then dilute it to 100 ml. with water.
- vi. Insert electrodes and take mV reading. Compare the latter with those from similarly-prepared standards and determine the p.p.m. fluoride in the sample.

This method allows fluoride to be determined over the range 500–50,000 p.p.m. with an accuracy of c.±11 per cent at the 95 per cent confidence level.

30–40 analyses can be carried out per 8-hour, man-day.

### INTERFERENCES

The fluoride electrode responds to hydroxyl ions, and when the concentration of the latter is greater than c. 10 per cent of that of the fluoride ions present, the results are not acceptable. In addition, low results can be obtained as a result of fluoride ions being removed from the system either as undissociated HF (this happens when the hydrogen ion concentration is high) or as complexes of  $\text{Si}^{4+}$ ,  $\text{Al}^{3+}$ ,  $\text{Fe}^{3+}$ , and  $\text{Be}^{2+}$ . Buffering minimises these interference problems.

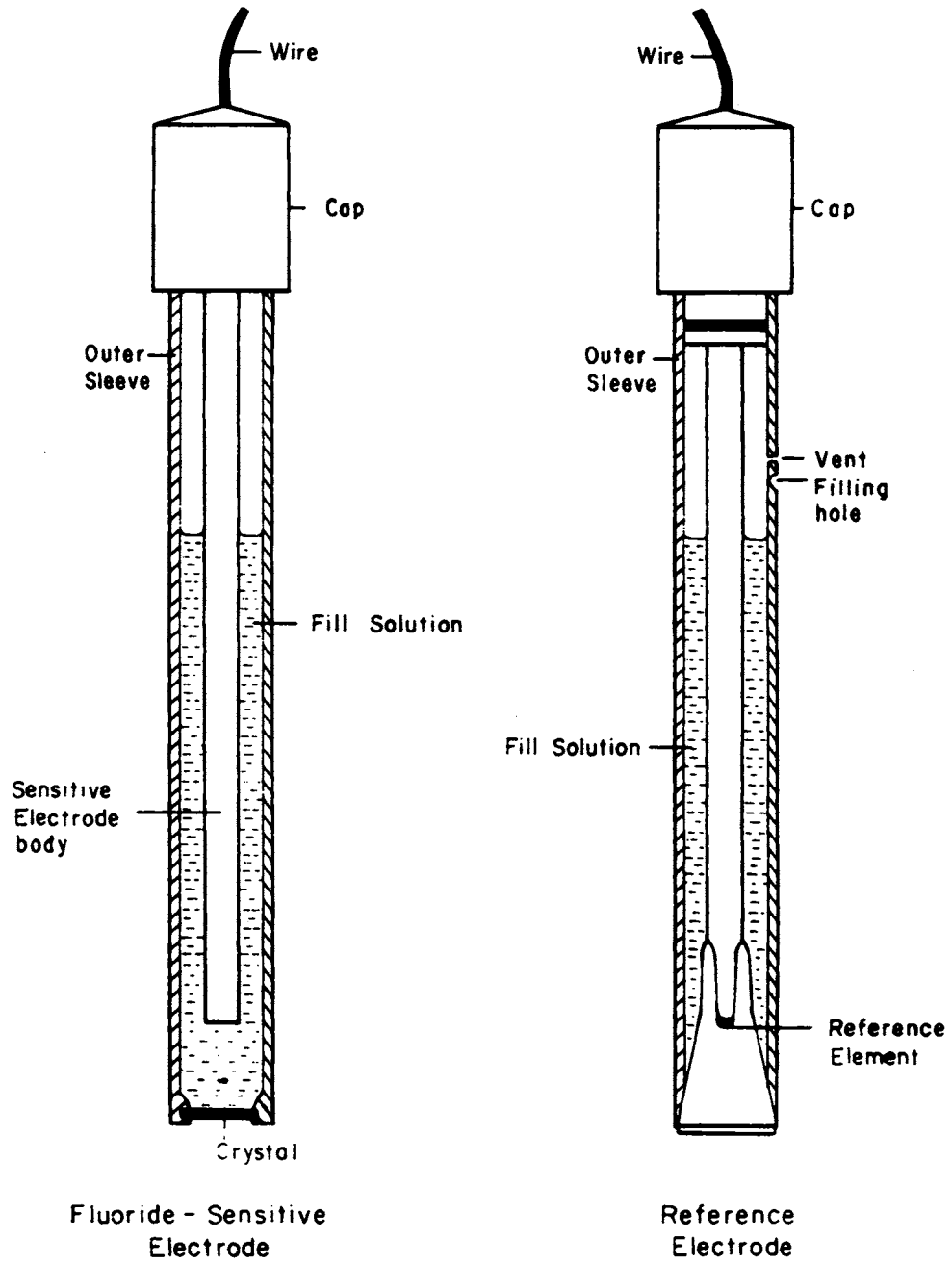


Fig. 1. Cross-section on Fluoride-Sensitive Electrode and Reference Electrode

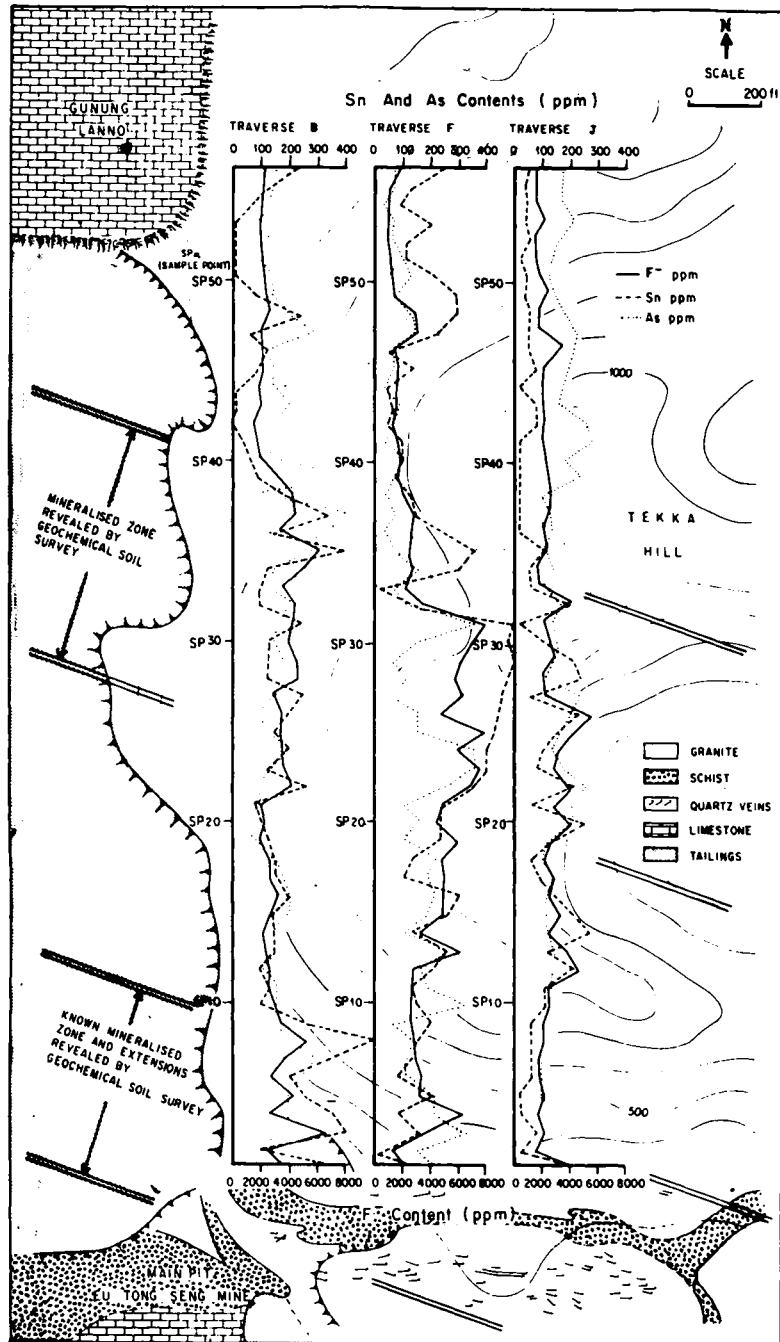


Fig. 2. The fluoride, tin and arsenic content of the minus-80-mesh fraction of B-horizon soil samples from Tekka Hill, Perak.

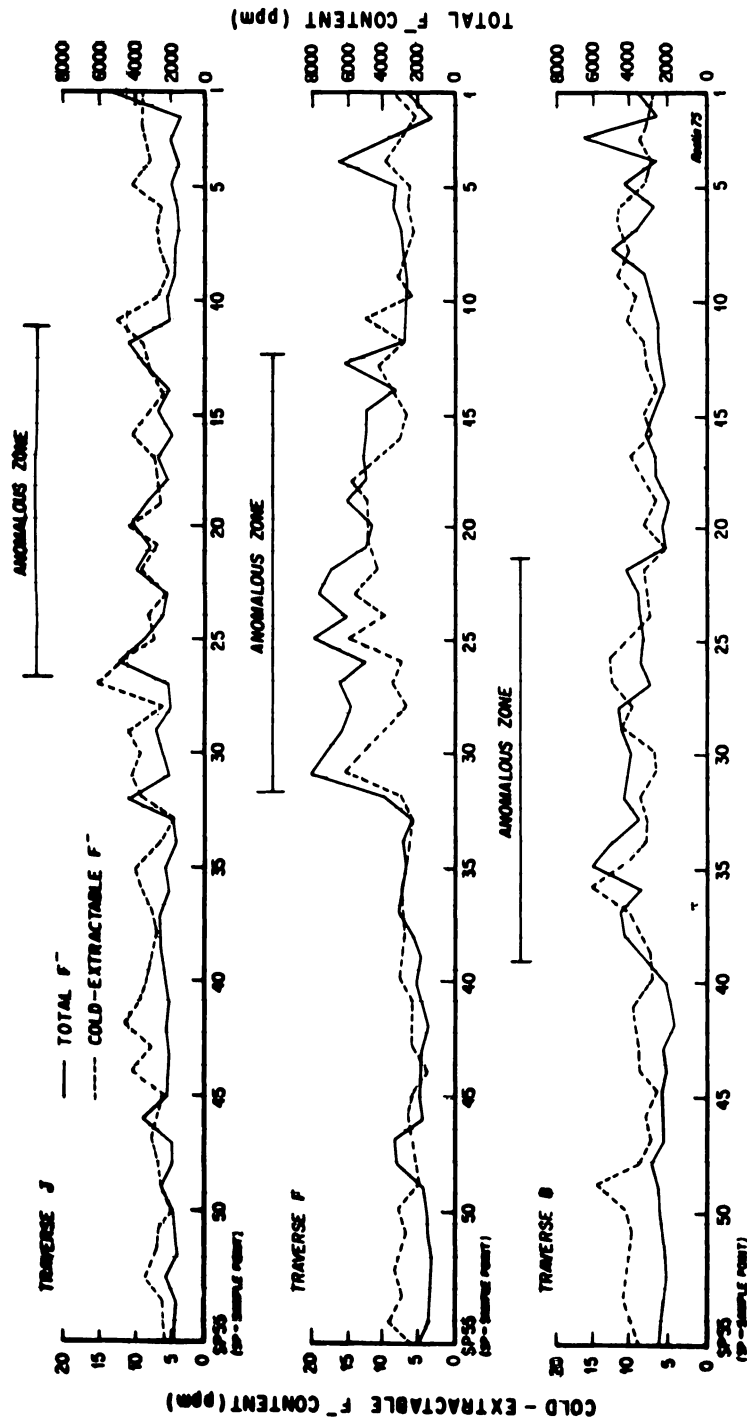


Fig. 3. The total and cold - extractable fluoride content of the minus-80-mesh fraction of B-horizon soil samples from Tekka Hill, Perak.

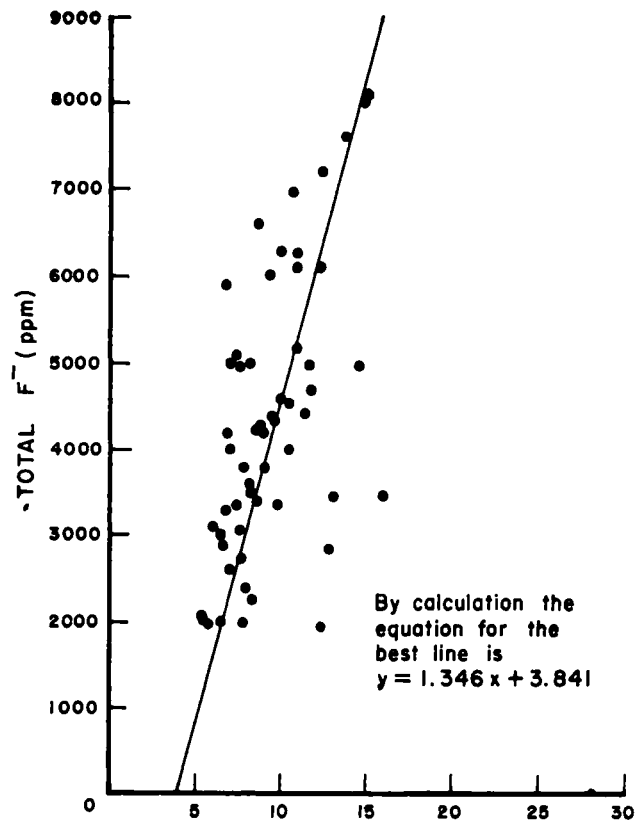


Fig. 4. Correlation between the total and cold-extractable fluoride content of the minus-80-mesh fraction of B-horizon soil samples from Tekko Hill, Perak.

## RESULTS OF THE TEKKA ORIENTATION SURVEY

Plots of the results obtained by analyzing the Tekka soils for tin and arsenic, both by Stanton's methods (1966, pp. 81–84, and 44–47) and for total fluoride, are provided in Fig. 2. The concentrations of all three vary more or less sympathetically, although in this area total fluoride appears to be a somewhat better path-finder for tin than arsenic is. Furthermore, over the anomalous zone there is a good correlation between total and cold-extractable fluoride (Fig. 3 & 4) and hence, in some localities, the less expensive and more rapid cold-extractable method can be used to advantage in an exploration programme. However, such a decision should only be taken after an appropriate orientation study had justified it.

Finally, in view of the common occurrence of anomalous concentrations of fluorine in and adjacent to tin deposits, where it is most prone to report as fluorite or in the micas, and because of the comparative ease with which the element can now be determined, it may soon become one of the more commonly used path-finder elements by those seeking tin deposits by geochemical methods.

## ACKNOWLEDGEMENTS

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