

A COMPARISON OF NEUTRON ACTIVATION DELAYED NEUTRON COUNTING VERSUS FLUOROMETRIC ANALYSIS IN LARGE-SCALE GEOCHEMICAL EXPLORATION FOR URANIUM

R.G. GARRETT, J.J. LYNCH
Geological Survey of Canada,
Ottawa, Canada

Presented by E.H.W. Hornbrook

Abstract

A COMPARISON OF NEUTRON ACTIVATION DELAYED NEUTRON COUNTING VERSUS FLUOROMETRIC ANALYSIS IN LARGE-SCALE GEOCHEMICAL EXPLORATION FOR URANIUM.

A comparison is made between uranium determined by fluorometric and delayed neutron activation methods for a regional geochemical reconnaissance in Saskatchewan. Control experiments demonstrate that manganese levels in excess of 1000 ppm in the lake sediment sample material cause serious quenching of uranium-induced fluorescence in the fluorometric analyses. The importance of this quenching is demonstrated in the reconnaissance data. Although anomalous patterns are not seriously modified if they coincide with areas of low manganese content it is demonstrated that regional patterns and relationships are significantly modified. Therefore interpretation of fluorometric data for uranium has to be interpreted with special care.

INTRODUCTION

Chemical methods of analysis, as distinct from various gamma-ray counting methods, have been used to aid in the geochemical exploration for uranium in Canada since the early 1960s, e.g. Chamberlain [1,2]; Smith [3]; Macdonald [4]; Meyer [5]; Smith and Lynch [6]; Morse [7]; Little and Durham [8]; Allan and Cameron [9]; Dyck [10]; and Hornbrook et al. [11]. Both government and industry have been active in exploration for uranium deposits using geochemical methods based on the collection and analysis of waters, stream and lake sediments, soils and rocks. At present the most common methods of analysis are fluorometric; some paper chromatographic methods are used, e.g. the Quebec Department of Natural Resources (pers. comm. G. Cockburn, 1975; Plamondon [12]). Delayed neutron activation analysis has been used in Canada on a large scale only since 1975. The major problem with the fluorometric methods of analysis are the quenching effects of Fe and Mn which lead to suppression of uranium-induced fluorescence, leading to erroneously low values being recorded. This suppressant effect is not encountered in delayed neutron activation analysis. This paper presents the results of a series of control experiments where increasing amounts of manganese were added to a series of uranium standards to determine the magnitude of the suppressant effect. Following this study 3844 centre-lake bottom sediment samples originally analysed for uranium by fluorometry (Hornbrook et al. [11]) were submitted for analysis by delayed neutron activation, the results of these two sets of analyses are compared.

FLUOROMETRIC METHOD OF ANALYSIS

The method of analysis was based on that described by Smith and Lynch [6], the major difference being in the sample dissolution which was modified for use with organic-rich lake

sediment. As the sample solution was also used for the determination of zinc, copper, lead, nickel etc. A 1-g sample weight was used to ensure sufficient sample solution. The 1-g sample is reacted with 6 ml acid mixture (4M HNO_3 -M HCL) in a test-tube overnight at room temperature. The test-tube is then placed in a water bath at room temperature and heated to 90°C . The digestion continues at this temperature for 2 h with occasional shaking. At the end of the digestion period the sample solution is cooled to room temperature, diluted to 20 ml and mixed.

A 100- μl aliquot of the sample solution (equivalent to 5 mg of the original sample) is transferred to a platinum dish (diam. 31.8 mm) and evaporated to dryness on a hot plate. The dish is then heated for a few seconds over a Fisher burner to destroy organic material. After cooling, a 3-g charge of carbonate-fluoride flux is added to the dish. This flux is composed of 45.5% Na_2CO_3 , 45.5% K_2CO_3 and 9% NaF . The platinum dish is placed in an electric furnace and the sample is fused for 10 min with periodic swirling to ensure a homogeneous melt. At the end of the fusion time the dish is removed from the furnace and allowed to cool for 20 to 30 min. The fused disc is then parted from the dish and placed in the fluorometer (Galvanck-Morrison model) for the fluorescence measurement.

For calibration, aliquots of a 0.1- $\mu\text{g}/\text{ml}$ uranium solution are carried through the procedure described in the previous paragraph. These aliquots correspond to 0.005, 0.01, 0.02, 0.04, 0.06, 0.08, 0.1 μg uranium. In actual analysis, if samples fall above 0.1 μg uranium they are repeated using a smaller sample aliquot. A reading of 0.1 μg uranium corresponds to 20 ppm uranium in the original dry sample. The control experiments were carried out by following the calibration procedure with the addition of varying amounts of manganese corresponding to desired ppm contents in a dry sample. The standard uranium solution used was derived from a stock solution, which in turn was prepared by dissolving $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (uranyl nitrate) in 4M HNO_3 .

DELAYED NEUTRON ACTIVATION ANALYSIS

The method of analysis, developed by Atomic Energy Canada Ltd., Commercial Products Division, is described in some detail by Boulanger et al. [13]. Briefly, the sample is irradiated in a Slowpoke reactor for 60 s, allowed to cool for 10 s and then counted for 60 s. The number of counts is a linear function of the number of micrograms of natural uranium in the irradiated sample.

When a sample containing uranium is bombarded with a neutron flux in a nuclear reactor fission of the uranium occurs. Some of the fission-product nuclides emit delayed neutrons. Because the delayed neutrons can be detected and selectively counted the total amount of uranium present can be readily determined by comparison to standard reference materials of known uranium content.

In practice a 1-g sample is weighed into a 7-dram polyethylene vial, capped and sealed. The irradiation is provided by the Slowpoke reactor with an operating flux of $1 \times 10^{12} \text{ cm}^{-2} \text{ s}^{-1}$. The samples are pneumatically transferred from an automatic loader, which can handle 50 samples at a time, to the reactor for the 60-s irradiation. After irradiation the samples are cooled for 10 s before pneumatic transfer to the counting facility which consists of six $^{10}\text{BF}_3$ detector tubes embedded in paraffin wax; samples are counted for 60 s and then discharged into a shielded storage container where they remain until they are safe to handle. As a minimum, calibrations are carried out twice a day using natural standards of known uranium content.

CONTROL EXPERIMENTS

Although both iron and manganese are known to cause quenching in fluorometric analysis (Price et al. [14]; Grimaldi et al. [15]; Michelson [16]; Centanni et al. [17]; and Ingles [18]) the control experiments were carried out with manganese alone. Manganese was chosen as in the

TABLE I. RELEVANT STATISTICAL PARAMETERS

	Range		Arith. mean	SD	C.V. %	Geom. mean	S.D.
Fe (%)	0.1	30.0	3.00	2.16	72	2.53	0.253
Mn (ppm)	30.0	89000.0	790.0	2673.0	338	495.0	0.318
LOI (%)	0.5	91.0	28.4	17.34	61	22.4	0.337
U _{Fluor} (ppm)	0.1	112.6	3.3	5.31	159	2.0	0.457
U _{DNA} (ppm)	0.2	100.0	6.1	6.03	98	4.9	0.273

Note: Table based on 3844 analyses; standard deviation quoted in \log_{10} units.

TABLE II. RANGE CONCENTRATION FACTOR (RCF) FOR IRON AND MANGANESE

	Log ₁₀ mean	Log ₁₀ SD	95% Limits of the range		RCF
Fe (%)	0.402	0.253	0.8	7.9	9.8
Mn (ppm)	2.695	0.318	118.0	2081.0	17.6

Note: Calculations based on geometric mean and \log_{10} standard deviation.

centre-lake bottom samples discussed in this paper manganese shows a greater variability than iron, Tables I and II. The range contrast factor (RCF) at the 95% limits of the range of the data is nearly twice as large for manganese relative to iron.

For the control experiment, uranium solutions corresponding to 2, 5, 7, 10, 15, 20 and 30 ppm in dry sample were prepared. From these additional solutions were prepared which correspond to manganese contents in the dry sample in the range 10 ppm to 50% following a semi-logarithmic interval, i.e. 10, 20, 50, 100, 200, 500 000 ppm. In addition to the 105 solutions thus prepared, blanks were also prepared corresponding to no uranium and all manganese contents and to no manganese and all uranium contents. The former series of blanks showed consistently zero uranium, and in the latter uranium levels were not significantly different from those obtained with 10 ppm manganese added. Each of the 105 solution had its apparent uranium content determined in triplicate, leading to a total of 315 determinations.

Figure 1 shows the curves drawn through the sets of 3 points for each known uranium content and varying manganese contents. The individual points are not shown for the sake of clarity. In some instances, i.e. 10, 15 and 20 ppm uranium, the observed contents were high in terms of the known content, these data were not corrected and are due to minor analytical errors. In the higher uranium contents the quenching effect of the manganese is apparent by the time 100 ppm manganese is present, at the lower levels of uranium quenching does not become apparent until somewhere between 100 to 1000 ppm manganese is present. The manganese has effectively completely quenched the uranium fluorescence by 10 000 ppm (1%) manganese for all levels of uranium.

To facilitate a comparison between the quenching effects of varying manganese content at the 7 different uranium contents between 2 and 30 ppm the ratio of observed value/true value was calculated for each of the 315 determinations. If the ratio exceeded unity it was set to unity. Figure 2 illustrates the behaviour of the ratio with increasing manganese content; only the curves for 2 and 30 ppm uranium are shown in order that the plot remains legible. The figure clearly

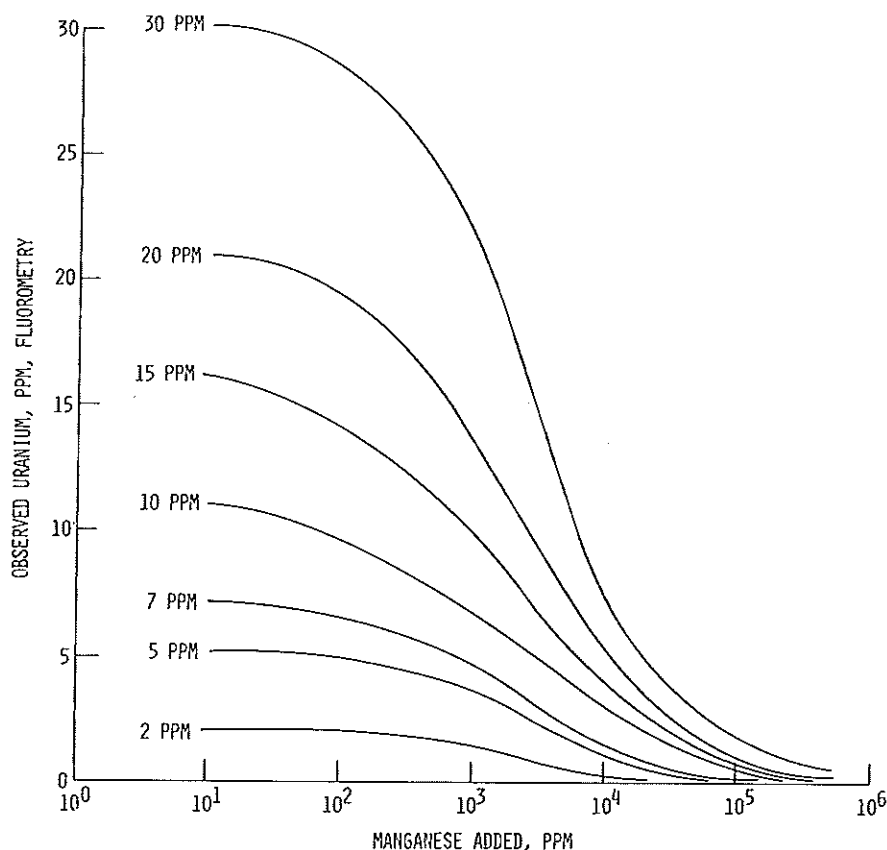


FIG.1. Fluorometric uranium versus manganese.

demonstrates that up to 100 ppm manganese the quenching effect is negligible; however, by the time manganese levels reach 1000 ppm the apparent uranium content is 75% of its true value. In the decade 1000–10 000 ppm manganese a further 50% of the uranium fluorescence is quenched, thus at 1% manganese the apparent level is only 25% of the true value.

It is clear from the foregoing that, if uranium exploration is being undertaken by geochemical methods and fluorometric analysis, the manganese content of the sample media is of critical importance. If the manganese contents of the sample media remain below 100 ppm and iron poses no problem fluorometric methods of analysis are perfectly adequate. However, as manganese increases, the problem becomes more severe and an alternative method of analysis, or a separation stage in a fluorometric scheme, should be investigated.

COMPARISON OF FLUOROMETRIC AND DELAYED NEUTRON ACTIVATION DATA

In 1974 a centre-lake bottom sediment geochemical reconnaissance survey was undertaken in the southeastern part of the Canadian Shield in Saskatchewan (Hornbrook and Garrett [19]). The fluorometric analysis method was used in this survey. Once all the data were accumulated it became apparent from a study of the iron and manganese data that the variable manganese contents of the samples could seriously hinder the interpretation of the uranium data. Therefore, the 3844 samples of the survey where uranium had been determined were submitted for delayed neutron activation analysis.

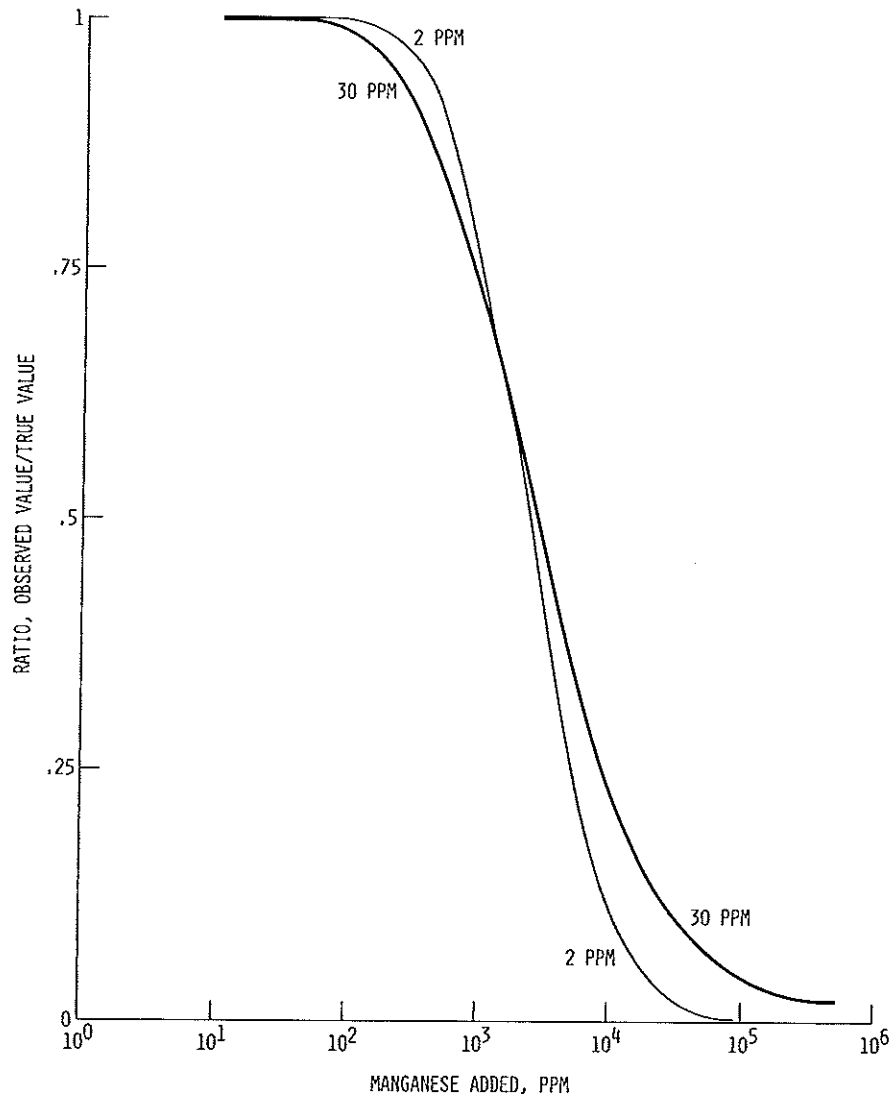


FIG.2. Observed value/true value versus manganese.

It could be argued that it is unrealistic to compare fluorometric uranium data based on a partial acid leach with "total" delayed neutron activation data. The centre-lake bottom sediments are very largely composed of organic ooze, various oxides and hydroxides and clay minerals. The detrital mineral content is small, especially for heavy detritals capable of carrying uranium in a form which could not be made available for fluorometric analysis. Such minerals as these are deposited in the near shore environment where streams carrying them in a high-energy state enter the low-energy state lake environment. Therefore, we believe the partial uranium released to be in fact a close approximation to the total uranium due to the physical and mineralogical nature of the sample material.

The data derived from the two methods of analysis are compared in Fig.3. The diagonal marks the line of equality, the majority of the data are below this line indicating that the delayed neutron activation method is in general giving higher uranium contents than the fluorometric method. A noticeable feature of Fig.3 is the bar-like cluster of points at 0.2 ppm uranium by

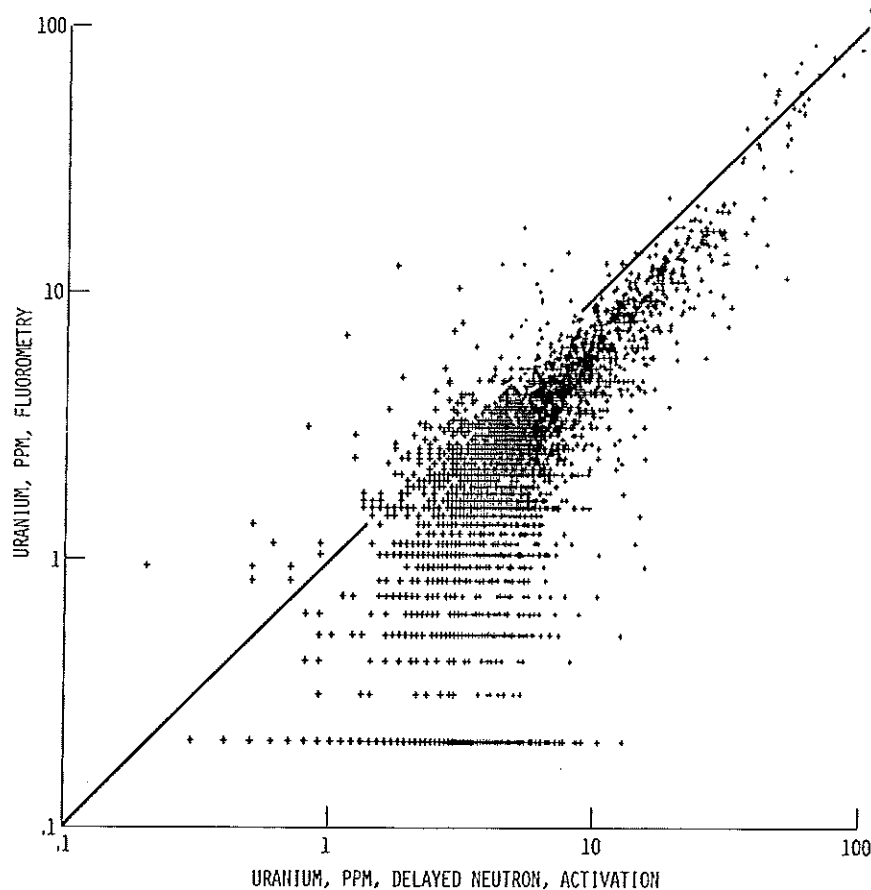


FIG.3. Fluorometric uranium versus delayed neutron activation uranium.

fluorometry; this is caused by the sensitivity of the fluorometric method. The sensitivity, or detection limit is 0.5 ppm in the solid and values less than this amount are arbitrarily set to 0.2 ppm for this method. The general increase in uranium as determined by the delayed neutron activation method can be ascribed to the absence of the quenching effects of the iron and manganese contents of the samples that caused depressed uranium contents to be observed by fluorometry. Of some importance in this particular case is the cluster of some 30 samples of high uranium content that lie close to the diagonal at levels in excess of 27 ppm uranium by fluorometry. At these levels the two methods of analysis give very similar results.

An alternative way to compare the two sets of data is via their frequency distributions (Figs 4 and 5). Both histograms and cumulative frequency plots are presented. In the histograms the positive skew of the data is far more evident in the delayed neutron activation data (Fig.5) than in the fluorometry data (Fig.4), which is modified by a higher proportion of lower values and some 9% of the data being below the detection limit. The same features are apparent on the cumulative frequency plots, especially the artificial termination of the plot by the fluorometric detection limit. A statistical comparison of the two cumulative frequency plots can be undertaken using the Kolmogorov-Smirnov statistic (Miller and Kahn [20]). The test yields a critical separation, at the 95% confidence level, of 0.031, this is exceeded between 0.2 to 15 ppm uranium indicating that the two distributions are significantly different, particularly at low levels.

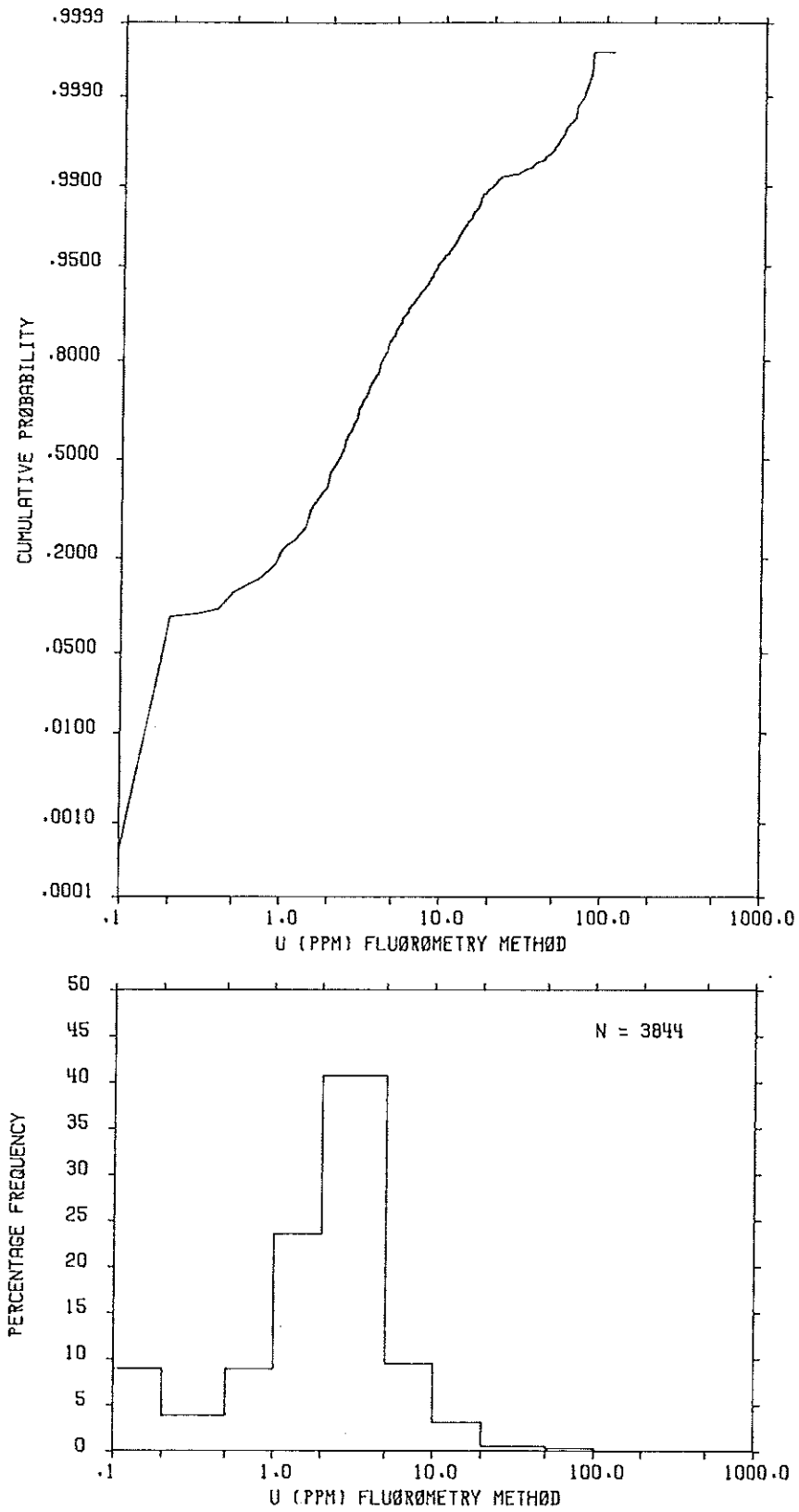


FIG.4. Frequency distribution of fluorometric data.

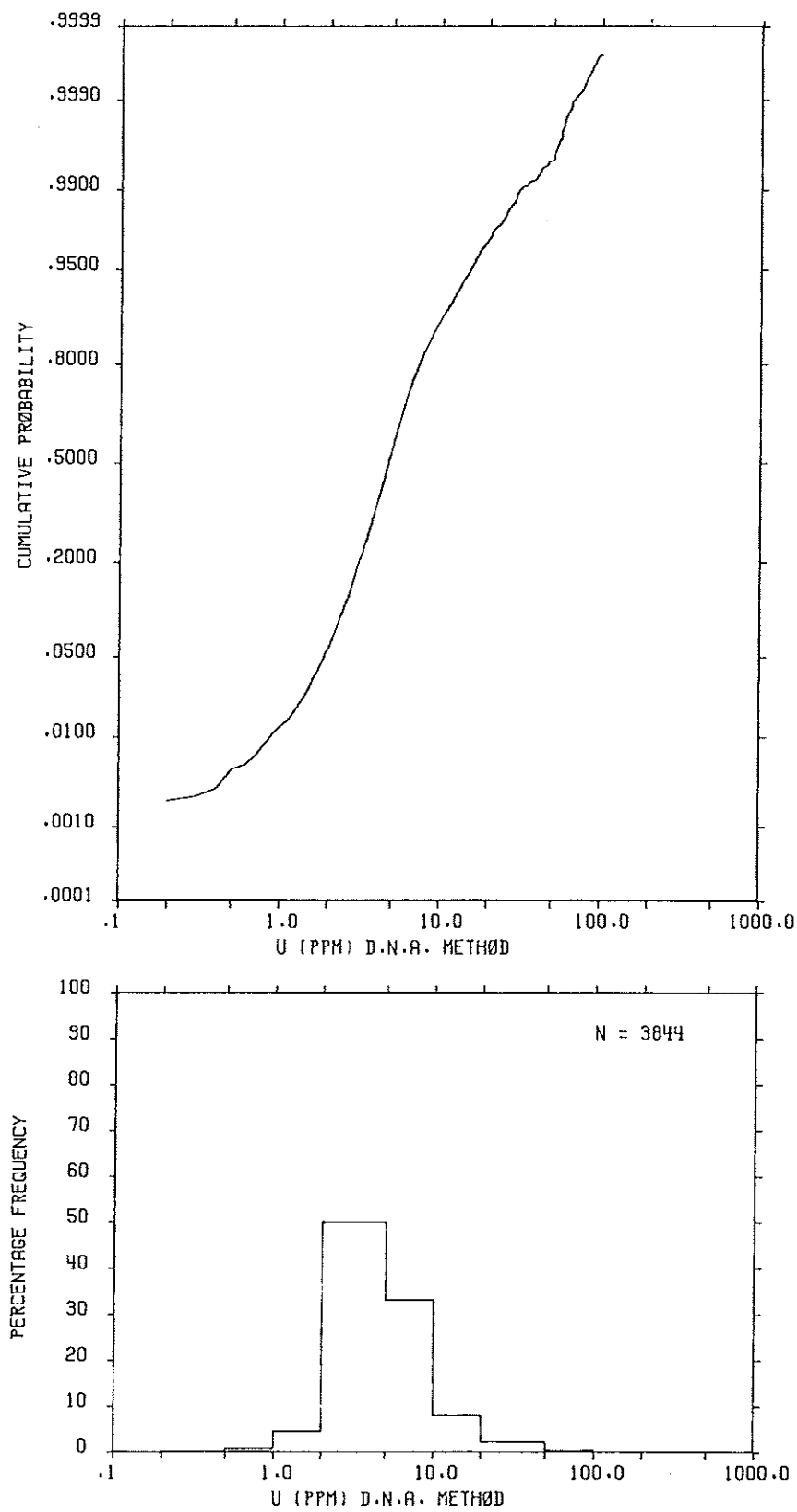


FIG.5. Frequency distribution of delayed neutron activation data.

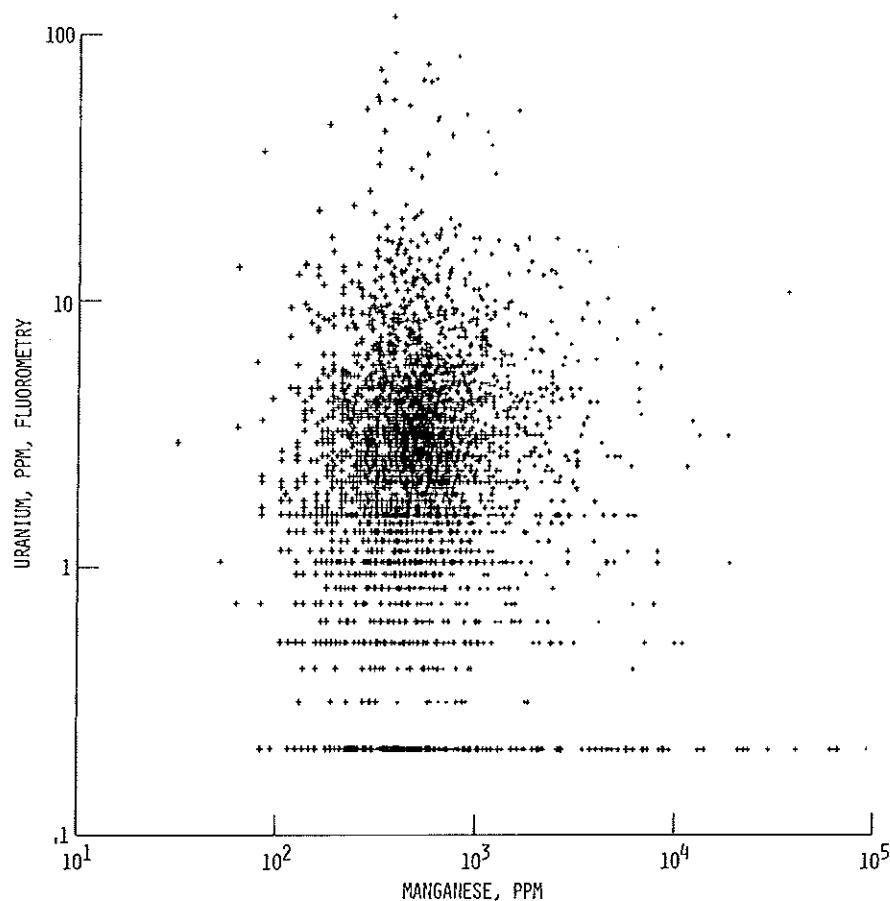


FIG.6. Fluorometric uranium versus manganese.

The actual effect of the manganese in the 3844 samples may be observed by comparing the two sets of uranium data each against the manganese data (Figs 6 and 7). The most noticeable features are the upwards movement of the centre of gravity of the data for delayed neutron activation and disappearance of the bar of fluorometric data equivalent to samples below the detection limit (Fig.6). The samples in the "sub-detection limit" group move up into the area of mean uranium content by delayed neutron activation; this is particularly noticeable for manganese levels greater than 5000 ppm where a definite projection into areas of high manganese at around 7 ppm uranium is observable (Fig.7).

IMPACT ON INTERPRETATION

It can be seen that the highest uranium values occur between 200 and 1000 ppm manganese (Fig.6). This is not modified by the new delayed neutron activation data; however, a considerable number of samples move up into the greater than 27 ppm uranium area first described with reference to Fig.3. In terms of the areal distribution of the data these samples build up the shoulders of the geochemically high areas but do not radically change the overall distribution pattern.

In interpretation of the fluorometric data various thresholds for selecting anomalous samples were chosen according to the rock type of the lake catchment basins. These thresholds varied from 7 to 18 ppm uranium, the mean of these, weighted by abundance of rock types, is 14 ppm; and mean plus 2 standard deviations for the complete set of fluorometric data is 16 ppm uranium.

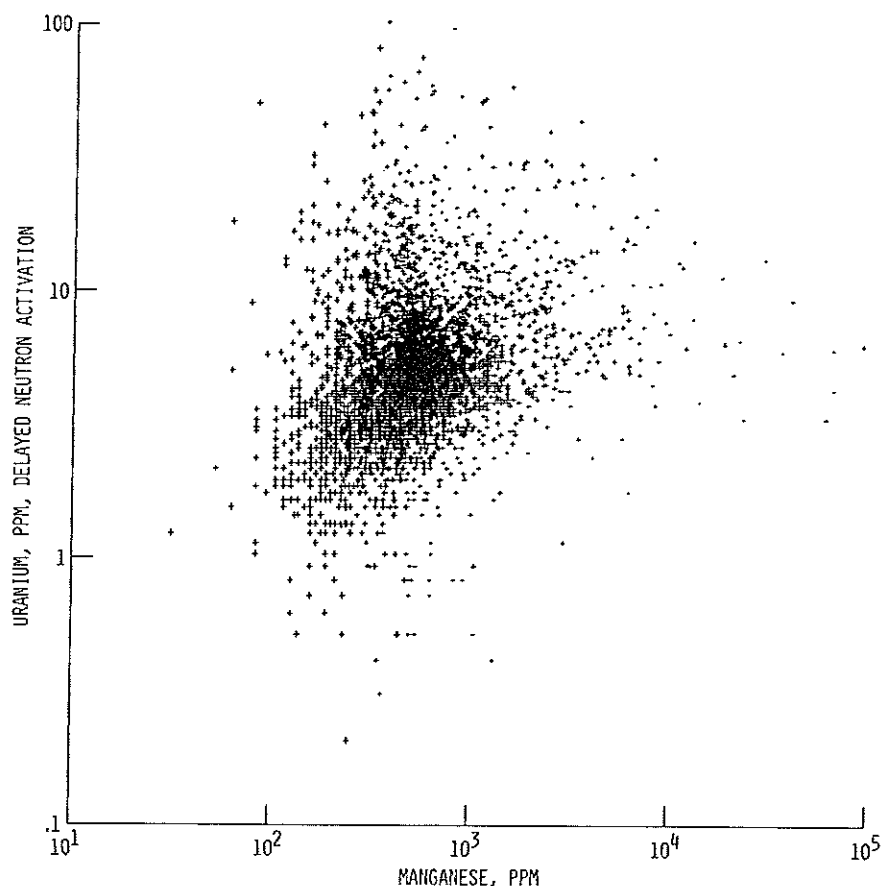


FIG. 7. Delayed neutron activation uranium versus manganese.

It is of interest that the mean plus 2 standard deviation level for the complete set of delayed neutron activation data is 17 ppm; the increase in mean being offset by a decrease in standard deviation to yield a result very similar to the 16 ppm of the fluorometric data. However, this comparison is misleading as the high standard deviation for fluorometric data is partly due to the 9% of the data set to 0.2 ppm as it fell below the detection limit. A second way is to use as a threshold for the delayed neutron activation data the same percentile as that corresponding to the weighted mean threshold for the fluorometric data, i.e. 97.8th percentile which corresponds to 22 ppm uranium, delayed neutron activation.

Some 61 samples are both greater than 14 ppm fluorometric and 22 ppm delayed neutron activation. An additional 19 are above the fluorometric threshold but below the delayed neutron activation threshold. Conversely there are 14 samples above the delayed activation threshold but below the fluorometric threshold. Therefore, the two methods of analysis lead to an additional 25% of data, above the unequivocal 61 samples, which may, or may not, be anomalous. These samples in the case of fluorometric uranium lie between the threshold and 22 ppm; and in the case of delayed neutron activation data between the threshold and 47 ppm. Thus, it can be seen that no new highly anomalous samples with values above 50 ppm U, delayed neutron activation, are created. Conversely this leads to the conclusion that the original fluorometric data, in the instance of this survey, was reasonably satisfactory for the detection of highly anomalous areas. However, this is solely due to the fact that in the anomalous areas of the Saskatchewan survey manganese levels are in general less than 1000 ppm. In terms of broad-scale regional geochemistry, where more subtle features are of interest and importance, the fluorometric data are clearly inadequate.

TABLE III. CORRELATION COEFFICIENTS BASED ON \log_{10} TRANSFORMED DATA, $n = 3844$

	Fe	Mn	LOI	U_{Fluor}	U_{DNA}
Fe	1.00	0.64	-0.21	0.10	0.33
Mn	0.64	1.00	-0.21	-0.02	0.29
LOI	-0.21	-0.21	1.00	0.11	-0.07
U_{Fluor}	0.10	-0.02	0.11	1.00	0.70
U_{DNA}	0.33	0.29	-0.07	0.70	1.00

Interpretation is rarely carried out in terms of only one chemical variable. Of particular interest in centre-lake bottom sediment surveys are the relations of various trace metals to iron, manganese and organic content as estimated by loss-on-ignition (LOI). These variables are measures of secondary environmental processes that can mask, or exaggerate, trace metal responses, thus confusing interpretation.

The correlation coefficients of \log_{10} transformed data are presented in Table III. Iron and manganese behave similarly, increasing together as insoluble hydroxides are precipitated on the lake floor; both these elements have an inverse relationship with LOI, indicating a gross compositional feature, i.e. as organics increase hydroxides decrease, and vice versa. The correlation of the fluorometric uranium data with iron and manganese is low relative to that for the delayed neutron activation data with those elements. It is proposed that this is due to the quenching effects on iron and manganese which inhibit data with both high fluorometric uranium and high iron and manganese. This is not a problem with delayed neutron activation data, and hence the higher correlation coefficients. The differences between the correlations of the two uranium analysis sets to LOI is explainable in the same terms. As iron and manganese rise fluorometric uranium values are inhibited by quenching, simultaneously LOI values are lower owing to the gross compositional changes noted above; the results of this is the positive correlation of fluorometric uranium with organic contents as measured by LOI. In reality there is a negative correlation of uranium (delayed neutron activation) with LOI indicating that uranium is preferentially adsorbed on to iron and manganese hydroxides relative to organic material. From the foregoing it is clear that advanced mathematical and statistical methods, e.g. factor or regression analysis, based on correlation matrices, should be used with considerable care for uranium data acquired by the fluorometric method.

CONCLUSION

The problems of iron and manganese quenching in the determination of uranium by fluorometry have been demonstrated. For a large reconnaissance lake sediment survey in Saskatchewan samples originally analysed for uranium fluorometrically were re-analysed by delayed neutron activation. The results are compared, the major features of the data do not change in serious fashion owing to the coincidence of the majority of high uranium samples with low manganese levels, i.e. < 500 ppm. However, the data presented reveal the interval of 1000–10 000 ppm manganese as covering the decade where the effects of quenching increase most rapidly; after 10 000 ppm (1%) manganese, fluorometric data should not be used. If geochemical surveys are to be undertaken in environments where manganese levels in excess of 1000 ppm are going to be frequently encountered the fluorometric method of analysis described in this paper should not be used. Lastly, significant

changes in the correlation matrix occur, even when much of the data lies below 1000 ppm manganese; therefore, sophisticated procedures based on correlation matrices should be used with care.

ACKNOWLEDGEMENTS

The authors wish to thank E.H.W. Hornbrook for critically reading the manuscript. Special thanks go to A.T. Maclaurin and G.E.M. Aslin who undertook the control experiment to provide the data presented on the manganese dependence of apparent uranium content.

REFERENCES

- [1] CHAMBERLAIN, J.A., Hydrogeochemistry of uranium in the Bancroft-Haliburton region, Ontario, *Geol. Surv. Canad. Bull.* 118 (1964) 19.
- [2] CHAMBERLAIN, J.A., Field and laboratory methods used by the Geological Survey of Canada in geochemical surveys; No. 7, A field method for determining uranium in natural waters, *Geol. Surv. Canad., Paper* 64-14 (1964) 8 pp.
- [3] SMITH, A.Y., Uranium in stream sediments in southeastern New Brunswick, New Brunswick Dept. Nat. Resources, Min. Res. Br., Inf. Circular 68-3 (1968) 4 pp.
- [4] MACDONALD, J.A., An orientation study of the uranium distribution in lake waters, Beaverlodge district, Saskatchewan, *Int. Geochem. Expl. Symp.* (2nd) 1968 (F.C. CANNEY, Ed.), *Q. Col. Sch. Mines* 64 No. 1 (1969).
- [5] MEYER, W.T., Uranium in lake water from the Kaipokok region, Labrador, *Int. Geochem. Expl. Symp.* (2nd) 1968 (F.C. CANNEY, Ed.), *Q. Col. Sch. Mines* 64 No. 1 (1969) 377-94.
- [6] SMITH, A.Y., LYNCH, J.J., Field and laboratory methods used by the Geological Survey of Canada in geochemical surveys, No. 11, Uranium in soil, stream sediment and water, *Geol. Surv. Canad., Paper* 69-40 (1969) 9 pp.
- [7] MORSE, R.H., Comparison of geochemical prospecting methods using radium with those using radon and uranium, *Geochem. Expl., Proc. 3rd Int. Canad. Inst. Min. Metall. (Special)* 11 (1971) 215-30.
- [8] LITTLE, H.W., DURHAM, C.C., Uranium in stream sediments in carboniferous rocks of Nova Scotia, *Geol. Surv. Canad., Paper* 70-54 (1971) 17 pp.
- [9] ALLAN, R.J., CAMERON, E.M., Uranium content in sediments, Bear Slave Operation, *Geol. Surv. Canad. Map* 9-1972 (1973).
- [10] DYCK, W., Geochemical studies in the surficial environment of the Beaverlodge area, Saskatchewan, *Geol. Surv. Canad., Paper* 74-32 (1974) 30 pp.
- [11] HORNBOOK, E.H.W., GARRETT, R.G., LYNCH, J.J., BECK, L.S., Regional lake sediment geochemical reconnaissance data, East-Central Saskatchewan (NTS 63M, 64D and parts of 63K, 63L, 63N, 73I, 73O, 73P, and 74A), *Geol. Surv. Canad., Open File Rep.* 266, 52 maps and 108 pp. (1975).
- [12] PLAMONDON, J., Rapid determination of uranium in geochemical samples by paper chromatography, *Econ. Geol.* 63 No. 1 (1968) 76-79.
- [13] BOULANGER, A., EVANS, D.J.R., RABY, B.F., "Uranium analysis by neutron activation delayed neutron counting", *Proc. 7th Ann. Symp. Canadian Mineral Analysts*, Thunder Bay, Ontario, 22-23 Sep. (1975).
- [14] PRICE, G.R., FERRETTI, R.J., SCHWARTZ, S., Fluorophotometric determination of uranium, *Anal. Chem.* 25, No. 2 (1953) 322-31.
- [15] GRIMALDI, F.S., MAY, I., FLETCHER, M.H., TITCOMB, J., Collected papers on methods of analysis for uranium and thorium, *US Geol. Surv. Bull.* 1006 (1954) 184 pp.
- [16] MICHELSON, C.E., The preparation of fluoride melts for use in the fluorometric method of uranium analysis, *U.S. Atomic Energy Commission Paper* HW-36831 (1955) 38 pp.
- [17] CENTANNI, F.A., ROSS, A.M., DE SESA, M.A., Fluorometric determination of uranium, *Anal. Chem.* 27, No. 11 (1956) 1651-57.
- [18] INGLES, J.C., Manual of analytical methods for the uranium concentrating plant, *Canad. Dept. of Mines Tech. Surv., Mines Br. Monograph* 866, Part II-U1 (1958) 1-41.
- [19] HORNBOOK, E.H.W., GARRETT, R.G., Regional geochemical lake sediment survey, East-Central Saskatchewan, *Geol. Surv. Canad., Paper* 75-41, 1976, in press.
- [20] MILLER, R.L., KAHN, J.S., *Statistical Analysis in the Geological Sciences*, John Wiley and Sons Inc., New York (1962) 483 pp.

DISCUSSION

K.J. WENRICH-VERBEEK: This research has long been needed in geochemical exploration. I should like to ask whether incomplete dissolution of the sample could account for fluorometry yielding lower values than delayed-neutron counting. That is, are you sure all of your sample, including silicates such as zircon, is going into solution?

E.H.W. HORNBROOK: Zircon, sphene and the like are not found in centre-lake bottom sediments in sufficient quantities to give rise to a problem of this nature.

L. LØVBORG: Have you considered the possibility that the values of some of the uranium determinations made by delayed-neutron counting might be a little too high because of interference with thorium in the samples? An error like this must be expected if the samples are irradiated in a mixed flux of thermal and fast neutrons.

E.H.W. HORNBROOK: Yes, this was considered by the staff of the Commercial Products Division of Atomic Energy of Canada Ltd., who carry out our uranium determinations. The data were not considered to be a "little too high" because of interference problems.

A. GRIMBERT: Once again I should like to defend the fluorometric technique for determining uranium; if manganese and iron are interfering elements (fluorescence inhibitors), one can easily eliminate them by paper chromatography. Moreover, with fluorometry one can determine mobile uranium (dissolving in dilute nitric acid), which is much more useful in geochemical prospecting than the determination of total uranium.

E.H.W. HORNBROOK: This is not the situation in centre-lake bottom sediment material, but it does apply in the case of stream sediments, soils etc. The procedure for removal of iron and manganese is relatively expensive and slow as well.

A.Y. SMITH: I am afraid you may have left the impression in the minds of your readers that the fluorometric method gives unreliable results and should not be used. Our project in Greece and the IAEA in general have been using the fluorometric method and recommending it to developing countries for their uranium prospecting programmes for several reasons: The fluorometric method is well within the capability of most countries to apply — in terms of both cost and simplicity. The method has general applicability, and if carefully used returns data of adequate reliability to outline significant "areas of interest" for uranium follow-up. The delayed-neutron method does none of these things. For most countries, the DNA method is out of the question from every point of view: They lack the necessary funds, reactors and skilled people to perform the analyses. As we have found in northern Greece, the *total* determination of uranium by any method (including the DNA method) may produce completely misleading uranium geochemical prospecting formation, except where it can be demonstrated that solution transport is the major or only mechanism of uranium dispersion at work. In northern Greece, we have found that only about 10% of the total uranium content of our samples can be extracted by hot concentrated HNO_3/HCl attack. The balance is present in resistate mineral phases and of no interest for geochemical prospecting purposes. I believe that for most parts of the world the same situation will be found. Thus, and in spite of the well-known quenching problems of the fluorometric method, I feel that it is widely applicable and can be used with confidence by workers in uranium geochemical prospecting. I regret to see it denigrated in this way.

E.H.W. HORNBROOK: It is most certainly not our intention to give readers the impression that the fluorometric method gives unreliable results in all instances. We want to warn, to awaken people to a problem which many may have forgotten in view of the wide acceptance and use of the fluorometric method. We do not exhort them to get involved in the DNA method. Luckily, in Canada, for large numbers of samples, the cost per analysis by fluorometry and DNA is competitive. However, we are the first to admit that this situation may be unique. We do state in our paper that in areas of high manganese and iron content the fluorometric method we describe should not be used. However, the fluorometric method has very many advantages, not the least being its suitability for use with partial dissolution methods. A separation stage may be introduced into the

procedure to remove the iron and manganese prior to preparation of the fusion disc. This procedure would be perfectly adequate, though admittedly costing some time and money, to ensure an improved quality of data in areas where the chemical dissolution used liberated significantly large amounts of manganese and iron from samples along with the uranium.

R.L. BRODZINSKI: Regarding the absolute accuracy of your DNA measurements, I would like to suggest a possible modification of the analytical procedure. First reduce the sample size by a factor of 10 to reduce the amount of neutron attenuation by the sample. Then, instead of irradiating for 60s, delaying 10s and counting 60s, irradiate for 6s, delay only 1s and count for 6s. Three such cycles will give you the original sensitivity in much less time. Alternatively, if you do not have the facilities for short cyclic irradiation, you can still use your original irradiation delay-count regime on the smaller sample and obtain the same sensitivity by gamma counting short-lived fission fragments such as ^{140}Cs (see my paper, IAEA-SM-208/50, these Proceedings).

A.Y. SMITH: It must be emphasized that Mr. Hornbrook is describing a very special environment, and also a particular dispersion system in which all the elements being measured, including uranium and manganese, enter the system in solution. In such a system you may be seeing an exceptionally strong relationship between manganese and uranium. It is becoming evident in many parts of the world that this close relationship is less common than previously supposed. In northern Greece, for example, we find an almost complete separation, geographically and geologically, between the base metal areas (in which areas manganese is an important element in the base metal association) and uranium areas.

E.H.W. HORNBROOK: The specific environment of lakes in the Canadian Shield may be unique whereas the solution mode of metal transport is not, nor is this really relevant to the problem. In any environment, anywhere in the world, problems may be encountered if the chemical dissolution of a sample releases large amounts of manganese and iron into solution with the uranium. The view that the manganese-uranium association is less common than had previously been thought is what might be expected on the basis of fluorometric data, as we have shown. However, as you well know there are areas in the world, such as the North American Appalachians, which are demonstrated manganese provinces containing known uranium occurrences. All that could be said on the basis of fluorometric data at this time is that the case is not proven.

A.Y. SMITH: You are correct in emphasizing the importance of quenching in the fluorometric method of uranium analysis and the quantitative data you have provided are welcome. The problem is perhaps not quite as serious as you suggest, however. The presence of 1000–2000 ppm Mn in the sample is readily seen by the blue to purple colour produced in the flux disc. When this occurs it is a simple matter to reduce the aliquot taken by half or less, and thus reduce the quenching. For example, using the Fig. 1 of your paper, a sample containing 20 ppm U and 10 000 ppm Mn would report about 5 ppm U. If 1/10 of the first aliquot is taken the uranium will report at about 12–13 ppm. Thus it is possible by simple means at least to reduce the problem. But as you point out, "the original fluorometric data, in the instance of this survey, were reasonably satisfactory for the detection of highly anomalous areas". Your explanation for this may be more universally applicable than you suppose.

E.H.W. HORNBROOK: You are quite right that quenching problems can be circumvented by taking a smaller aliquot, thereby reducing the total amount of manganese and iron present in the fusion. However, your example of 20 ppm U and 10 000 ppm Mn is misleading. Such a sample is obviously anomalous. The problem area is the one close to threshold, e.g. 4 ppm U and 10 000 ppm Mn. If the original detection limit was 0.2 ppm U and a 1/10 dilution is used the detection limit on re-analysis will be 2 ppm U. In the first run the apparent U would be 1 ppm and after a dilution it would be 3 ppm. In the second case one is working close to the detection limit, now 2 ppm U, in an area where confidence in the analytical method is lessening. There is the possibility that the uranium present could be entirely diluted away to below the increasing detection limit.