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Fluorometric Determination of Uranium in Environmental Materials

by

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ABSTRACT

This report describes the fused fluoride pellet fluorometric method of uranium determination used at the Los Alamos Scientific Laboratory for the measurement of uranium in environmental samples with concentrations as low as 0.1 ppb total U. These analytical techniques are routinely used in the analysis of thousands of samples of soils, natural waters, and various biological materials.

I. INTRODUCTION

The analytical chemistry of uranium was extensively investigated as part of the Manhattan Project.¹ Since then a wide variety of measurement techniques have been developed: gravimetric,² volumetric,³ colorimetric,⁴ coulometric,⁵ polarographic,⁶ alpha-particle counting,⁷ activation analysis,⁸ fission track counting,⁹ and chemical separation techniques.¹⁰

The early description of the fluorometric procedure for uranium, as given by Price et al.,¹¹ forms the basis for the techniques described herein, although a number of specific improvements have been made. Fluorometric uranium determination has been used routinely for analyzing medical and biological materials,¹² as well as for natural waters¹³ and geological samples.¹⁴ The latter applications are becoming increasingly important for uranium prospecting by hydrogeochemical methods¹⁵ on the national scale, where rapid, accurate, and cost-effective analysis for uranium at the ppb level is required for tens of thousands of samples.

Fluorometric procedures have also been applied to the determination of Be,¹⁶ B,¹⁷ Cd,¹⁸ Ga,¹⁹ Ge,²⁰ Li,²¹ rare earth elements,²² Zn,²³ and Zr,²⁴ as well as the application of fluorometry in vitamin analysis.²⁵ This list is not exhaustive. Many improvements have been made in the fluorometric determination of these elements, the description of which is beyond the scope of this document.

II. EXPERIMENTAL

A. Apparatus and Reagents

1. Platinum dishes (Fig. 1)
2. Pellet maker (Fig. 1 and 5)
3. Nichrome wire screen (Fig. 1)
4. Extraction apparatus (Fig. 3)
5. Fusion burner (Fig. 2 and 4)
6. Air and propane regulators (Fig. 4)
7. Timer (Fig. 4)
8. Fluorometer (Fig. 6)
9. Sodium Fluoride (fluorometric grade MCB)
10. Other reagents all of which are analytical-reagent-grade chemicals.

B. Preparation of Standards

National Bureau of Standards, SRM (Standard Reference Material) 950a (U_3O_8) is used as the primary standard. A 1.179-g portion of the SRM is dried for 1 h in an open crucible at $900^\circ C$, cooled in a desiccator, dissolved in a solution of 10% nitric acid (HNO_3) and 1% sulfuric acid (H_2SO_4), and diluted to 1 liter. This primary standard has a uranium concentration of 1.00 mg/ml which can be further diluted to match concentrations expected in samples being analyzed. When a new primary standard is prepared, it is compared against the existing standard and submitted to other groups for intralaboratory analysis.

C. Method

An aliquot of a liquid sample, or of a solution of a solid sample, is diluted and acidified to contain between 5 to 500 ng U/ml in 5 to 10% HNO_3 . If ions are present which will interfere with the uranium fluorescence, an aliquot of the diluted sample is salted with aluminium nitrate [$Al(NO_3)_3 \cdot 9 H_2O$] solution and the uranium is extracted into ethyl acetate ($CH_3CO_2CH_2CH_3$). Aliquots of either the diluted sample or the extracted sample are removed and transferred onto pellets of lithium fluoride-sodium fluoride (LiF-NaF) flux in platinum dishes. The pellets are then dried, fused, and allowed to cool, forming buttons. The fluorescence of the button is measured using a Galvanek-Morrison fluorometer.

D. Preparation of Samples

Soil samples are ground to -100 mesh and mixed to produce a homogenous sample. An aliquot of the soil is weighed and transferred into a 250-ml teflon beaker, then digested using 20 ml of HNO_3 and 50 ml of HF. During acid digestion the solution is evaporated to dryness on a hot plate and wet ashed with HNO_3 and hydrogen peroxide (30% H_2O_2) to dissolve any carbonaceous material which might be present. After digestion the sample is diluted and acidified so the final volume contains 10% HNO_3 .

Biological samples are dried to constant weight, ground and mixed, and then treated in the same manner as the soil samples. Aqueous samples received for uranium analysis are filtered and acidified to contain 1% HNO_3 .

E. Interferences

The quenching effect on uranium fluorescence is of great concern when working with samples containing very low levels of uranium and unknown quantities of interfering ions. A list of the more abundant elements of the earth's crust, and their effect on fluorescence, is shown in Table I. Solutions with a range of 0:1, 25,000:1, 100,000:1, and 200,000:1 of element to uranium were pipetted directly onto fluoride pellets which were dried, fused, and cooled to determine fluorescence and thus detect the quenching effect of the added elements. The elements that had quenching effects decreased fluorescence quantitatively with increased element concentration. The trend of the quenching effect of the elements tested at the highest concentration ratio was $Cr > Fe > Cu > Ni > Zn > Ti > Al > Ca > K$. Loss of fluorescence was 100% with Cr, 77% with Fe, 50% with Cu and Ni, and 36% with Zn. Pellet discoloration appears to be indicative of high levels of quenching ions. When the direct method is used and discolored pellets are produced, the samples should be rerun using the $CH_3CO_2CH_2CH_3$ extraction procedure.

F. Extraction Procedure

Ten milliliters of aluminium nitrate solution [$2g Al(NO_3)_3 \cdot 9 H_2O/ml$] is placed in a screw cap extraction 25-ml vial. An aliquot of sample is added that will yield an $CH_3CO_2CH_2CH_3$ solution that contains between 5 and 500 ng U/ml. Two to ten milliliters of $CH_3CO_2CH_2CH_3$ are pipetted rapidly into the vial, which is capped and shaken vigorously for 1 min. The sample volume and the amount of $CH_3CO_2CH_2CH_3$ used is dependent on the expected uranium concentration.

The four elements with the highest quenching effect were added to uranium standards and the standards analyzed to determine the effectiveness of the extraction procedure.

In evaluating the efficiency of the extraction procedure, the volume of sample analyzed is critical. If the quantity of $\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$ is kept constant as the sample volume is increased, the efficiency of the extraction decreases. This study indicates that 1 ml is the maximum sample volume which should be used in the extraction with 10 ml of $\text{Al}(\text{NO}_3)_3 \cdot 9 \text{H}_2\text{O}$. Figures 7 and 8 show the results obtained when the volume of standard was increased from 1 to 6 ml using two different concentrations of uranium. The expected fluorescence decreased with increased volume of standard, indicating incomplete extraction of the uranium into the $\text{CH}_3\text{CO}_2\text{CH}_2\text{CH}_3$. This was probably due to inefficient salting capabilities of the aluminum nitrate solution with volumes greater than 1 ml of standard.

G. Preparation of Pellets for Fusion

Twenty platinum dishes are placed on a nichrome wire screen according to the pattern shown in Figs. 1 and 9. A flux pellet is formed, using a pellet maker, from a mixture of 98% NaF - 2% LiF, and placed in each platinum dish. The flux pellets have an approximate weight of 55 mg each. The desired aliquots of the samples and standards are pipetted onto the flux pellets using a volume between 0.05 ml and 0.25 ml depending upon the suspected uranium concentration. (The standards used on each plate should have uranium concentrations that bracket the uranium concentration of the samples on the sample plate.) After all the standards and samples have been pipetted, the nichrome screen and the dishes are moved onto a hot plate and allowed to dry for 15 to 20 min. The flux pellets must dry completely before fusion or the flux will splatter from dish to dish causing cross contamination of the samples.

H. Fusion Procedure

After the nichrome screen is placed on the fusion burner, the pilot light is ignited and the air flow is adjusted to 1000 SCFH and approximately 80 SCFH of propane is added to the gas stream. The timer is set for 2 min and the propane flow is slowly readjusted until the flame is of the proper height and temperature as shown in Fig. 10. Flame height diminishes as the screen becomes heated, and the procedure for properly adjusting the flame requires experience before it can be done routinely. After 90 s the propane flow is decreased to approximately 50 SCFH, and the bubbles which have formed at the bottom of the dishes should rise and dissipate (Fig. 11). After 2 min fusion time, the propane and then the air are shut off.

The large variation in fluorescence of standards due to fluctuation during fusion prompted detailed investigation of fusion control. Very small changes in parameters of the gases during fusion were found to change the calibration curve as much as 90%. Therefore, the effect of varying the fusion time was studied at three measured temperatures (1190°C Fig. 12, 1260°C Fig. 13 and 1420°C Fig. 14). Fluorescence in samples fused at 1260°C appears to be rather insensitive to variations in the duration of the fusion; therefore, this is obviously the optimum temperature to fuse the pellets.

The results show that running single pellet standards and samples and assuming a constant calibration curve can introduce substantial error in analysis of the samples. The review of literature on uranium analysis revealed that many laboratories run single pellet fusions giving little consideration to variation during fusion. Another method evaluated was one in which multiple fusions used only one concentration for the standards run on the sample plate. This incorrectly assumes that the standard curve passes through the origin, and this circumstance is frequently not true. The methods reviewed did not indicate any

method that might be used for quality control for plate-by-plate or pellet-by-pellet fusion. The method that has been developed in this study eliminates the guessing of fusion conditions that has led to many erroneous results. It consists of running each fusion plate with the samples in duplicate and the two different concentrations of standards in triplicate. This method takes into account the variables that take place during fusion, and eliminates the uncontrollable problem of slope variation of the calibration curve as a function of fusion conditions.

As soon as flux solidification is complete the screen is removed from the burner and placed on a heat-resistant surface. Since the cooling rate affects the fluorescence of the pellets, it is important to follow the same procedure in cooling each set of fused buttons.

1. Calculations

After cooling the plate of fused buttons for 15 min, each pellet is measured using a Galvanek-Morrison Fluorimeter (Fig. 6) at the lowest scale. A calibration curve is calculated by plotting instrument readings in microamperes vs concentration of uranium of the two standards. The calibration curve for this study was calculated using a program which used a weighted least squares fit with the associated uncertainties of the calibration points if two or more standard concentrations have been used. Allowing for the intensity and uncertainty of readings, the final uranium concentration and its uncertainty can be calculated. Uncertainty of the readings can be determined two different ways. One is to take the variations of the readings on each set of duplicate samples of a fusion plate, the other is to determine variation on a large number of standards and apply an average variation to each sample and allow only a maximum spread in readings. A listing of the computer program is presented in the Appendix.

J. Results and Discussions

Uranium analyses of low-level natural water samples from Alaska and New Mexico were made by neutron activation²⁶ and fluorimetry to evaluate the accuracy of this procedure. The results of the comparison are shown in Table II. All analyses are standardized using solutions prepared from National Bureau of Standards Reference Material 950a.

Filtered and unfiltered samples were analyzed to evaluate potential differences introduced by suspended particulate matter. The unfiltered samples are analyzed by taking 20 ml of the sample to dryness, dissolving the residue in 10% HNO_3 and pipetting directly onto the flux pellet. The filtered samples were filtered using 0.45 μm MF-millipore (mixed esters of cellulose) filters. After filtration, 20 ml of the filtrate was evaporated to dryness, and the sample residue was dissolved in 10% HNO_3 and pipetted directly onto the flux pellet.

The samples with uranium concentration above 0.3 ppb generally agree within the analytical uncertainties; but both the filtered and unfiltered samples showed higher variation below the 0.3-ppb level. Samples with uranium concentrations less than 0.3 ppb are very close to the detection limits of the procedure, which probably accounts for the high variation.

The accuracy of this procedure was studied using one National Bureau of Standards SRM (Coal Fly Ash # 1633) and two International Atomic Energy Agency Reference samples (#467 and #25). Different dissolution techniques were implemented in analyzing the samples to determine if one might prove superior. In general, the three dissolution techniques worked equally well (see Table III). The samples with the higher uranium concentrations were diluted enough that quenching ions had little effect on the direct method. The low standard in Table III had little dilution which accounts for the low results probably due to quenching.

As a measure of accuracy, the recovery percentage is calculated using the following formula: % Recovery = $\frac{\text{Measured Value}}{\text{Actual Value}} \times 100$. As a measure of precision, twice the standard deviation (2 σ) from the mean of replicate values is determined (each group of six is considered one replicate group). A mean for all analysis (excluding the deviant fly ash) and a mean value for only those samples dissolved in HF-HNO₃ is reported in Table IV for each parameter. Each value has associated with it a 2 σ which is a measure of the population distribution.

$$\sigma = \sqrt{\frac{\sum_{i=1}^N (x_i - \bar{x})^2}{N-1}} \quad \text{and a } 2 \sigma_{\bar{x}} \left(\sigma_{\bar{x}} = \frac{\sigma}{\sqrt{N}} \right), \text{ which}$$

is a measure of how well the mean value is known.

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REFERENCES

1. Rodden, C. J. and J. C. Warf, National Nuclear Energy Series, Div. VIII, 1, "Analytical Chemistry of the Manhattan Project," 1950, pp. 122-135.
2. Duval, C., Anal. Chim. Acta 3, 335 (1949).
3. Sill, C. W. and H. E. Peterson, Atomic Energy Commission report BM-R1-4882 (June 1952).
4. Crouthamel, C. E. and C. E. Johnson, Anal. Chem. 24, 1780 (1952).
5. Carson, W. N., Anal. Chem. 25, 466 (1953).
6. Bloche, E., P. Leveque, and H. Provisor, Bull. Soc. Chem. France 16, 831 (1949).
7. Campbell, E. E., B. M. Head, and M. F. Milligan, Los Alamos Scientific Laboratory report LA-1920 (June 1955).
8. Makintosh, W. D. and R. E. Jervis, AEC of Canada, Ltd., report AECL-481 (April 1957).
9. Carpenter, B. S. and C. H. Cheek, Anal. Chem. 42, 121 (1970).
10. Rodden, C. J., Anal. Chem. 25, 1598 (1953).
11. Price, G. R., R. J. Ferretti, and S. S. Schwartz, Anal. Chem. 25, 322 (1953).
12. Neuman, W. F., R. W. Fleming, A. B. Carlson, and H. Glover, J. Biol. Chem. 173, 41 (1948).
13. Thatcher, L. L. and F. B. Barker, Anal. Chem. 29, 1575 (1957).
14. Adams, J. A. S. and W. J. Maeck, Anal. Chem. 26, 1635 (1954).
15. Boyle, R. W., E. H. W. Hornbrook, R. J. Allan, W. Dyck, and A. Y. Smith, "Hydrochemical Methods - Application in the Canadian Shield", presented at CIM 73rd Annual General Meeting, Quebec, Canada, April 1971.
16. Laitinen, H. A. and P. Kivalo, Anal. Chem. 24, 1467 (1952).
17. White, C. E., A. Weissler, and D. Busker, Anal. Chem. 19, 802 (1947).
18. Evcim, N. and L. A. Reber, Anal. Chem. 26, 836 (1954).
19. Bradacs, L. K., F. Feigl, and F. Hecht, Microchem. Acta 1954, 269 (1954).
20. Raju, N. A. and G. G. Rao, Nature 174, 400 (1954).
21. White, C. E., M. S. Fletcher and J. Parks, Anal. Chem. 23, 478 (1951).
22. Prizibram, K., Nature 139, 329 (1937).
23. Merritt, L. L., Ind. Eng. Chem. Anal. Ed. 16, 758 (1944).
24. Alford, W. C., L. Shapiro and C. E. White, Anal. Chem. 23, 1149 (1951).
25. Kodicek, E., Analyst 72, 385 (1947).
26. Gladney, E. S., J. W. Owens and J. W. Starnes, Anal. Chem., in press, 1976.

TABLE I
QUENCHING EFFECT OF URANIUM FLUORESCENCE

	Readings are in Microapphes	
	Direct	Extracted
10 ngU/Pellet	.72 ±.03	
" + 25 µg Ca	.71 ±.02	
" + 50 µg Ca	.71 ±.02	
" +100 µg Ca	.67 ±.04	
" +200 µg Ca	.65 ±.01	
10 ngU/Pellet	.63 ±.02	
" + 25 µg Al	.61 ±.03	
" + 50 µg Al	.61 ±.03	
" +100 µg Al	.50 ±.04	
" +200 µg Al	.56 ±.01	
10 ngU/Pellet	.52 ±.02	
" + 25 µg K	.49 ±.02	
" + 50 µg K	.55 ±.02	
" +100 µg K	.57 ±.03	
" +200 µg K	.56 ±.01	
10 ngU/Pellet	.63 ±.02	
" + 25 µg Ti	.63 ±.05	
" + 50 µg Ti	.62 ±.02	
" +100 µg Ti	.62 ±.03	
" +200 µg Ti	.52 ±.02	
10 ngU/Pellet	.65 ±.03	.74 ±.03
" + 25 µg Fe	.45 ±.03	.72 ±.05
" + 50 µg Fe	.37 ±.01	.70 ±.04
" +100 µg Fe	.23 ±.01	.70 ±.10
" +200 µg Fe	.15 ±.01	
10 ngU/Pellet	.56 ±.04	.77 ±.04
" + 25 µg Cu	.49 ±.01	.69 ±.04
" + 50 µg Cu	.40 ±.01	.74 ±.02
" +100 µg Cu	.32 ±.03	.74 ±.02
" +200 µg Cu	.23 ±.01	
10 ngU/Pellet	.67 ±.02	.71 ±.03
" + 25 µg Ni	.52 ±.03	.68 ±.01
" + 50 µg Ni	.43 ±.01	.71 ±.02
" +100 µg Ni	.31 ±.02	.67 ±.05
" +200 µg Ni	.28 ±.03	
10 ngU/Pellet	.60 ±.03	.73 ±.03
" + 25 µg Cr	.24 ±.02	.69 ±.05
" + 50 µg Cr	.16 ±.01	.69 ±.05
" +100 µg Cr	.08 ±.01	.64 ±.05
" +200 µg Cr	.01 ±.01	
10 ngU/Pellet	.62 ±.02	
" + 25 µg Zn	.61 ±.01	
" + 50 µg Zn	.55 ±.03	
" +100 µg Zn	.45 ±.03	
" +200 µg Zn	.39 ±.02	

TABLE II
URANIUM CONCENTRATIONS IN NATURAL WATERS (ppb)

		Acidified, Unfiltered		Acidified, Filtered	
		RNA	Fluorometry	RNA	Fluorometry
Alaska - 1	1	0.44±0.09	0.26±0.05	0.74±0.09	0.53±0.08
	2	0.60±0.10	0.26±0.05	0.47±0.06	0.50±0.08
	3	1.4 ±0.1	1.67±0.09	1.4 ±0.2	1.7 ±0.1
	4	0.04±0.04	0.08±0.08	0.22±0.05	0.17±0.17
	5	0.22±0.06	0.17±0.17	0.11±0.05	0.04±0.02
	6	0.30±0.07	0.30±0.10	0.26±0.05	0.23±0.05
	7	0.26±0.07	0.23±0.12	0.10±0.05	0.13±0.04
	8	0.05±0.05	0.14±0.07	0.03±0.05	0.02±0.02
	9	0.31±0.06	0.15±0.06	0.31±0.05	0.41±0.15
	10	0.27±0.07	0.00±0.00	0.21±0.05	0.02±0.02
	11	0.05±0.05	0.11±0.08	0.02±0.04	0.02±0.02
	12	0.17±0.08	0.04±0.08	0.15±0.05	0.02±0.02
New Mexico - 1				24. ±2.	20. ±3.
	2			11. ±1.	0.9 ±1.0
	3			9.5 ±0.0	9.7 ±0.9
	4			2.3 ±0.2	2.0 ±0.3

TABLE III
PROCEDURE ACCURACY USING REFERENCE SAMPLES

	NBS 91633	IAEA 9467	IAEA 925
	ppm U	ppm U	ppm U
Reported values	11.6±0.2	119±12	1187±50
1) Teflon Beaker	12.3±0.9	126±13	1220±160
2) Glass Beaker	13.0±2.4	114±11	1100±80
3) Na ₂ O ₂ /NaOH Fusion	14.0±4.9	111±8	1020±50
4) Direct Teflon Beaker	5.7±1.0	123±6	1090±35
1) 10 ml Nitric Acid, 30 ml Hydrofluoric Acid.			
2) 10 ml Nitric Acid, 5 ml Sulfuric Acid, 5 ml Hydrofluoric Acid.			
3) 5 g Sodium Peroxide, 2 g Sodium Hydroxide in Nickel crucible @ 1000°C.			
4) 10 ml Nitric Acid, 30 ml Hydrofluoric Acid bypassing ethyl acetate extraction.			

TABLE IV
QUALITY CONTROL DATA FOR URANIUM ANALYSIS

No. of Samples	% Recovery All Samples	HF-HNO ₃	% from Mean of All Samples	Replicates HF-HNO ₃
	54	10	11	6
$\bar{x}$	102%	10%	19%	19.5%
2σ	39%	21%	18%	18%
2σ ₂	5%	5%	5%	5%

Fig. 1. Platinum dish arrangement on nichrome screen.

Fig. 2. Fletcher Fusion Company.

Fig. 3. Extraction apparatus.

Fig. 4. Fusion apparatus.

Fig. 5. Flux pellet apparatus.

Fig. 6. Fluorometer and fused pellets.

Fig. 7. Fluorescence change due to volume change.

Fig. 8. Fluorescence change due to volume change.

S₁ - Standards (low value) 3 per plate.
 S₂ - Standards (high value) 3 per plate.
 #1-#7 Samples 2 per sample per plate.

Fig. 9. Fusion plate arrangement.

Fig. 10. First stage of fusion 1.5 min.

Fig. 11. Second stage of fusion 0.5 min.

Fig. 12. Fluorescence change due to change in fusion time at 1190°C.

Fig. 13. Fluorescence change due to change in fusion time at 1260°C.

Fig. 14. Fluorescence change due to change in fusion time at 1420°C.

APPENDIX A

PROGRAM IN BASIC LANGUAGE USED FOR CONCENTRATION CALCULATIONS

LIST

75-11-05. 12.52.45.
PROGRAM LINRES

```
00100 PRINT "MAKE A LEAST-SQUARES FIT TO DATA WITH A STRAIGHT LINE"
00110 PRINT
00120 PRINT "DESCRIPTION OF PARAMETERS"
00130 PRINT
00140 PRINT
00150 PRINT "X=ARRAY OF DATA POINTS FOR INDEPENDENT VARIABLES"
00160 PRINT "Y=ARRAY OF DATA POINTS FOR DEPENDENT VARIABLES"
00170 PRINT "SIGMA=ARRAY OF STANDARD DEVIATIONS FOR Y DATA POINTS"
00180 PRINT "N=NUMBER OF PAIRS OF DATA POINTS"
00190 PRINT "M=MODE=DETERMINED METHOD OF WEIGHTING LEAST-SQUARES FIT"
00200 PRINT "    +1 (INSTRUMENTAL) WEIGHT=1/(SIGMA(X)^2)"
00210 PRINT "    0=NO WEIGHTING, WEIGHT=1."
00220 PRINT "    -1=(STATISTICAL) WEIGHT=1/(X^2)"
00230 PRINT
00240 PRINT "A=INTERCEPT OF FITTED STRAIGHT LINE"
00250 PRINT "A1=SIGMA B=STANDARD DEVIATION OF A"
00260 PRINT
00270 PRINT "B=LOPE OF FITTED STRAIGHT LINE"
```

```

00280 PRINT "B1=SIGMA B=STANDARD DEVIATION OF B"
00290 PRINT
00300 PRINT " R=LINER CORRELATION COEFFICIENT"
00310 PRINT
00330 PRINT
00340 S=S1=S2=S3=S4=S5=0
00350 PRINT "NUMBER OF POINTS?      MODE?"
00360 INPUT N,M
00370 PRINT "NUMBER OF POINTS = "N,"MODE = "M
00380 PRINT
00390 PRINT
00400 DIM X(36),Y(36),K(36)
00410 PRINT " NO.      X      Y      SIGMA "
00420 FOR I=1 TO N
00430 PRINT
00440 INPUT X(I),Y(I),K(I)
00450 PRINT I,X(I),Y(I),K(I)
00460 IF K<0 THEN 490
00470 IF M=0 THEN 510
00480 IF M>0 THEN 530
00490 W=1/Y(I)
00500 GOTO 540
00510 W=1
00520 GOTO 540
00530 W=1/(K(I)+2)
00540 S=S+W
00550 S1=S1+W*X(I)
00560 S2=S2+W*Y(I)
00570 S3=S3+W*X(I)*X(I)
00580 S4=S4+W*X(I)*Y(I)
00590 S5=S5+W*Y(I)*Y(I)
00600 NEXT I
00610 PRINT
00620 PRINT
00630 PRINT "SUM = " S
00640 PRINT "SUM X = " S1
00650 PRINT "SUM Y = " S2
00660 PRINT "SUM X+2 = " S3
00670 PRINT "SUM X*Y = " S4
00680 PRINT "SUM Y+2 = " S5
00690 PRINT
00700 REM " CALCULATE COEFFICIENTS AND STANDARD DEVIATIONS"
00710 PRINT
00720 PRINT " CALCULATE COEFFICIENTS AND STANDARD DEVIATIONS "
00730 PRINT
00740 PRINT
00750 D=S*S3-S1*S1
00760 A=(S3+S2-S1*S4)/D
00770 B=(S4+S-S1*S2)/D
00780 IF M<0 THEN 810
00790 IF M=0 THEN 830
00800 IF M>0 THEN 810
00810 V=1
00820 GOTO 850
00830 C=N-2
00840 V=(S5+A*A+S+B*B+S3-2*(A*S2+B*S1-A*B*S1))/C
00850 A1=SQR(ABS(V*S3/D))
00860 B1=SQR(ABS(V*S4/D))
00870 R=(S+S4-S1*S2)/SQR(ABS(D*(S+S5-S2*S2)))
00880 PRINT "INTERCEPT EQUALS "A,"WITH A STANDARD DEVIATION OF " A1
00890 PRINT
00900 PRINT "SLOPE EQUALS " B,"WITH A STANDARD DEVIATION OF "B1
00910 PRINT
00920 PRINT "LINEAR CORRELATION COEFFICIENT IS " R
00930 PRINT
00940 PRINT "READING IS ?      WITH A STANDARD DEVIATION OF ? "

```

```

00945 PRINT
00950 INPUT C,C1
00955 IF C=9999 THEN 310
00960 C2=(C-A)/B
00970 D1=C2+(((C1/C)+2+(B1/B)+2)+0.5)
00980 PRINT
00990 PRINT " READING IS" C, "WITH A STANDARD DEVIATION OF "C1
01000 PRINT " CONCENTRATION OF "C2, "WITH ERROR OF "D1
01010 GOTO 945
01020 STOP
01030 END
READY

```