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AUTOMATION OF DATA COLLECTION AND
COMPUTATION FUNCTIONS FOR
MONOCHROMATIC X-RAY
ABSORPTION ANALYSIS

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UNION
CARBIDE

OAK RIDGE Y-12 PLANT
OAK RIDGE, TENNESSEE

prepared for the U.S. ATOMIC ENERGY COMMISSION
under U.S. GOVERNMENT Contract W-7405 eng 26

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FOR MONOCHROMATIC X-RAY ABSORPTION ANALYSIS**

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ABSTRACT

A small, dedicated computer was interfaced to the spectrogoniometer and timer-scaler units of a monochromatic X-ray absorption analysis apparatus to perform the functions of data collection, computation, and a printout of the results.

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SUMMARY

Semiautomatic control of an X-ray system used for monochromatic X-ray absorption analysis was achieved by interfacing a small, dedicated computer to the spectrogoniometer and scaler units of the X-ray instrument. The computer controlled the functions of setting the spectrogoniometer angles, starting and stopping the scalers, accepting the scaler data, calculating the sample results, and printing these results in final form via Teletype.

Supplementary software was provided for calculating the necessary constants in the X-ray absorption equation.

INTRODUCTION

The monochromatic X-ray absorption analysis method, as used in the Oak Ridge Y-12 Plant,^(a)(1 - 5) required close attention to the operation of the instrument and extensive manual calculation to obtain the results. Measurement of the absorption of X rays at wavelengths on either side of an absorption edge of the element of interest was accomplished using an X-ray spectrometer as a means of selecting the desired X-ray wavelengths. The X rays passing through the sample in a preset time were counted by a scintillation detector and associated electronics. Calculation of the element concentration by a derived X-ray absorption equation involved the difference of the logarithms of ratios of X-ray counts through water to X-ray counts through the sample at two wavelengths. With manual desk calculators and logarithm tables, much time was required and many opportunities for error were present. In order to simplify and speed up the analysis, a small, dedicated computer appeared feasible to control the instrument, acquire data, and calculate the results.

(a) Operated by the Union Carbide Corporation's Nuclear Division for the US Atomic Energy Commission.

CONTROL SYSTEM FOR AN X-RAY ABSORPTION APPARATUS

GENERAL OPERATION OF THE SYSTEM

Interconnections of the semiautomated control system are outlined in diagrammatic form in Figure 1. A liquid sample is placed in a sample cell in the collimated beam of the X-ray tube. The attenuated X rays passing through the sample are dispersed by the analyzing crystal (NaCl) such that essentially monochromatic X rays pass through the exit slit to the scintillation detector.

Information concerning the sample is manually fed to the computer from the Teletype console. Upon completion of the entry, the goniometer angle is positioned by the goniometer drive motor by signals received from the computer through the interface. Correct angle positioning is monitored through signals from the encoder.

Goniometer angles are first set at the low-angle, high-energy, high-absorption region adjacent to (within 0.3°) an absorption edge of the element being analyzed and designated commonly as Angle 1. The goniometer indicates the angle of the detector (mounted on the goniometer arm) from the incident X-ray beam and is twice the Bragg angle of rotation of the sodium chloride analyzing crystal. X rays reaching the detector at the Angle 1 setting are counted for a preset time, as controlled by the timer, and the accumulated counts transferred to the computer for storage and printout by the Teletype. Upon completion of three counts at Angle 1, the computer commands a change to Angle 2, the high-angle, low-energy, low-absorption side of the chosen element absorption edge. After accumulating three X-ray counts at Angle 2, the computer calculates the results which are printed by the Teletype, thus completing the analysis.

SYSTEM HARDWARE

A block diagram of the system hardware is presented in Figure 1. The computer used in the system is a PDP-8/L unit with 4096 memory locations.

Figure 1. PRINCIPAL COMPONENTS OF THE AUTOMATED X-RAY ABSORPTION SYSTEM.

The system interface was designed to provide control signals or data transfer between the computer and four major components. The four components include a pulse motor for driving the X-ray spectrogoniometer, an encoder to provide angular position feedback to the computer, control and data transfer circuitry for a timer and scaler, and an operator control panel.

The pulse motor used is a 200-steps-per-revolution type that is appropriately geared to drive the X-ray spectrogoniometer. The encoder is a quadrature-output type of 1,000 pulses per revolution and includes a zero reference pulse. A quadrature decoder with an output of two counts per quadrature cycle of the encoder is used to provide angular position feedback pulses to the computer. The timer is used to gate the scaler and allow the scaler to accumulate counts during a preset time interval. At the end of the preset time interval, the timer stops the scaler count accumulation and signals the computer that the scaler data are ready to be transferred to the computer. The six-digit scaler data are stored in the scaler in binary-coded decimal and transferred to the computer in a bit-parallel, word-serial format under program control. Data from both the encoder and scaler are entered into the computer by programmed instructions executed in response to the computer program interrupt facility. The operator control panel consists of an element (angle pair) selector switch and indicator, and an on-line/off-line switch. The element selector switch directs the computer program flow to the test angles required for the specific element under test. The on-line/off-line switch is tested by the computer to determine if the angle settings and timer/scaler control will be handled by the computer or done manually. An off-line setting requires all angles to be set manually and scaler data to be entered by Teletype. This feature was incorporated to enable the computer to accept data from any source through the Teletype input. Detailed interface logic diagrams are presented in the Appendix.

Photographs of the entire unit, the motor-driven goniometer, and the control panel consisting of the computer, interface power supply, and high-speed reader are provided in Figures 2 through 4.

SYSTEM SOFTWARE

The concept for the software included provision for ready adaptability to changing needs. To accomplish this objective, a standard programming language, FOCAL^(b) 1969, was chosen as a medium for the input of data, calculations, and output of results.

The use of the FOCAL language permits great flexibility in the calculation and printout formats to meet changing needs without resorting to lengthy revision and recompilation of the instrument control program. Certain unneeded functions were eliminated from the basic FOCAL language; eg, the sine, cosine, arc tangent, and analog-to-digital converter functions. This deletion released computer memory locations for storing instrument control instructions.

Program Assembly Language (PAL) was used in writing instructions for controlling the instrument functions. A flow chart of the program is provided in Figure 5. A binary-coded

(b) Registered trade mark of the Digital Equipment Corporation.

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Figure 2. OVERALL VIEW OF THE SEMIAUTOMATED X-RAY ABSORPTION INSTRUMENT. (Shown from Left to Right are the Counting Panel, Spectrogoniometer, and Computer/Interface Control Unit)

tape was prepared to load the instrument control instructions into the computer as an overlay to the FOCAL 1969 program. This overlay tape includes the instrument instructions as substitutions for the unneeded functions of FOCAL.

The FOCAL program for operator input of data, calculation, and printout of results gives a printout from a sample analysis, as given in Figure 6. Sample data, as seen in Figure 6, are entered via Teletype in response to typed queries. Following entry of the sample data, the computer commands that goniometer Angle 1 be set and three X-ray counts be taken followed by a change to Angle 2 with three additional counts. As soon as these six counts are completed, computation is made and the sample results printed in terms of grams of element per milliliter of solution analyzed and also as grams of element per gram of the original sample.

In the case of two aliquants of a sample, the second aliquant weight is requested with subsequent repeat of the angle setting and counting routines. Computations and printout for two aliquants include not only grams-per-milliliter and average grams-per-gram results, but

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Figure 3. X-RAY SPECTROGONIOMETER. (Note the Drive Motor/Reduction Gear Box Mounted on the Left Front and the Encoder on the Right Front)

also the deviation between aliquants as a percent of the average result. Calculation of the analytical results is by command of the FOCAL program instructions using the sample data and accumulated sample counts in the following X-ray absorption equation:

$$C_V = K_1 \log \frac{R_1}{S_1} - K_2 \log \frac{R_2}{S_2}, \quad (1)$$

where:

C_V represents the concentration of the element being analyzed in terms of the grams of element per milliliter of solution,

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Figure 4. CONTROL CABINET. (Unit Consists of the Computer, Interface, Power Supply, and High-Speed Reader)

Figure 5. FLOW CHART OF THE INSTRUMENT CONTROL PROGRAM.

G
 INST #:1
 ANY CHANGES?:Y
 NEW REF?:Y
 REF 1:495077
 REF 2:399357
 NEW CONST?:Y
 K1:0.031902
 K2:0.028791

REQ #:999999
 R1 = 495077
 R2 = 399357
 K1 = 0.031902
 K2 = 0.028791

1 OR 2 ALIQ?:2
 VOL :50
 SEC DIL?:Y
 ML USED:7
 DIL VOL:25

G WT:66.7486
 T WT:36.2038
 CNT ANG 1 :105989
 :106392
 :106144
 CNT ANG 2 :186659
 :184979
 :186547
 G/ML = 0.011781

G WT:68.1191
 T WT:37.6158
 CNT ANG 1 :106009
 :105587
 :106355
 CNT ANG 2 :186468
 :185970
 :185959
 G/ML = 0.011811

AVE G/G = 0.069009
 % DEV = 0.3881

Figure 6. PRINTOUT OF THE X-RAY ABSORPTION ANALYSIS RESULTS (Underlined Items are Entered by the Operator in Response to Typed Queries; the Remaining Printout is at the Instruction of the Computer Program)

K_1 and K_2 the experimentally determined constants characteristic of the sample type and sample cell,

R_1 and R_2 the mean reference (water) counts accumulated in a preset time at appropriate Angles 1 and 2, and

S_1 and S_2 the mean sample counts accumulated in a preset time at Angles 1 and 2.

From the concentration of the element in grams per milliliter, the concentration in grams of element per gram of original sample is calculated from the equation:

$$C_w = C_v \frac{V}{N} \frac{V_s}{V_p}, \quad (2)$$

where:

C_w represents the concentration of the element in grams per gram of sample,

V the volume of the sample after preparation and initial dilution,

N the net weight of the sample taken,

V_s the final volume of the secondary dilution, and

V_p the volume of the primary dilution taken for the secondary dilution.

Provision is made in the program for storing two sets each of water reference counts and equation constants simultaneously such that this information is immediately available for calculations for the automated instrument or for a manually operated X-ray instrument where all other data are input via the Teletype. Ringing of the bell at the conclusion of the sample analysis and calculations calls attention to the analyst that the instrument is ready for the next sample.

When loading programs into the computer, the complete FOCAL 1969 program and the FOCAL overlay containing substitute instructions for instrument control are loaded from binary-coded tapes via a high-speed reader. Address and starting of the computer is at the normal FOCAL memory

address of 0200 octal. Subsequent loading of the FOCAL language input/output and calculation program is from an ASCII-coded tape via the Teletype reader.

SUPPLEMENTARY SOFTWARE

As an aid in calculating the constants used in Equation 1, a computer program was written in XTRAN (an extended FORTRAN) language to be used on a time-sharing computer.^(c) These constants are obtained by substituting X-ray intensity readings of several standard solutions of the element of interest into Equation 1. From pairs of simultaneous equations, at least one of which must be for an impure solution,⁽²⁾ K_1 and K_2 are calculated.

Each equation for a pure solution is solved simultaneously with each equation for an impure solution. Provision is made to use either two or three impure standard solutions and two pure standard solutions yielding either four or six pairs of simultaneous equations for solution. In response to typed queries, the concentration (gms element/ml) and X ray counts at Angles 1 and 2 are entered for the water reference and for each standard solution. From these data, the average X-ray counts for each standard at each angle, the K_1 and K_2 constants with the ratio of K_1 and K_2 from each pair of simultaneous equations, and the average K_1 and K_2 values are computed and printed. The average K values are checked by calculating back to the concentration of the standards from the X-ray counts. Any large variation in the K_1 to K_2 ratios, the calculated standards concentrations, or a positive or negative bias toward one end of the concentration range indicates possible errors. The values used in calculating sample results; ie, average constants and average water reference counts, are typed at the bottom of the sheet for ready reference at the instrument. A typical printout of the program results is presented in Figure 7.

No doubt the constants computation could be written in FOCAL language for calculation at the instrument, but insufficient memory locations in the dedicated computer core prevented this approach. A similar time-sharing program was written for the case of two impure standards and either two or three pure standards.

LABORATORY EXPERIENCE WITH THE AUTOMATED X-RAY INSTRUMENT

Operation of the computer-controlled X-ray absorption instrument in routine analyses over a period of several months has proved its value. The automated system has become a favorite with analysts because of its speed, freedom from need for close attention, ease of operation, and reliability. Experience to date has shown that maintenance of the automated equipment is minimal. Thirty-five samples in duplicate can be analyzed readily in an eight-hour shift on the automated system. The inclusion of a call-bell signal in the operating program upon completion of a sample gives the analyst freedom to perform duties of sample preparation or taking data on other X-ray instruments until his attention is needed. With fewer details requiring close attention, the automated X-ray absorption analysis is much less hectic and tiring to the operating analyst than manual operation and calculation. Savings of

(c) Com-Share, Inc; Ann Arbor, Michigan.

2 OR 3 IMPIRE STANDARDS? 3

WHEN ASKED, TYPE DATA IN THIS FORMAT FOR EACH STANDARD.
USE 0 FOR H2O CONC. PUT 'SPACE' BETWEEN EACH NUMBER.

C0NC(G/ML) ANG 1 CNTS(3) ANG 2 CTS(3)

H2O 0 830104 831206 829002 690446 690923 689969
PUR 1 .010 84767 85179 85255 436733 436459 436523
PUR 2 .008 131970 132447 133061 475235 474823 474820
IMP 1 .007 99178 98597 98905 284679 285173 284134
IMP 2 .006 124423 123852 123337 295708 295568 296473
IMP 3 .005 150212 149915 150327 299669 299710 300068

C0NC	AVE CT1	AVE CT2
0.0000	830104	690446
0.0100	85067	436572
0.0080	132493	474959
0.0070	98893	284662
0.0060	123871	295916
0.0050	150151	299816

K1 PO.0100 : IMP0.0070 = 0.012474	
K2 PO.0100 : IMP0.0070 = 0.011760	K1/K2= 1.0607
K1 PO.0100 : IMP0.0060 = 0.012452	
K2 PO.0100 : IMP0.0060 = 0.011651	K1/K2= 1.0687
K1 PO.0100 : IMP0.0050 = 0.012476	
K2 PO.0100 : IMP0.0050 = 0.011772	K1/K2= 1.0598
K1 PO.0080 : IMP0.0070 = 0.012400	
K2 PO.0080 : IMP0.0070 = 0.011582	K1/K2= 1.0706
K1 PO.0080 : IMP0.0060 = 0.012382	
K2 PO.0080 : IMP0.0060 = 0.011494	K1/K2= 1.0772
K1 PO.0080 : IMP0.0050 = 0.012411	
K2 PO.0080 : IMP0.0050 = 0.011640	K1/K2= 1.0663

	C0NC	% DEV
PUR 1 =	0.009981	-0.2
PUR 2 =	0.008015	0.2
IMP 1 =	0.007004	0.1
IMP 2 =	0.005984	-0.3
IMP 3 =	0.005012	0.2

K1 AVE = 0.012432

K2 AVE = 0.011650

H2O AVE CNT 1= 830104 CNT 2= 690446

Figure 7. PRINTOUT OF THE COMPUTER CALCULATED VALUES OF THE X-RAY ABSORPTION EQUATION CONSTANTS.

time and effort are realized in collecting data and in calculating and checking the results prior to reporting the results of the analyses. Significantly fewer errors in transcribing the data and calculations have been noted. Such errors are time consuming and often result in a needless reanalysis of samples. The printout of results directly onto sample work cards serves as a permanent record of analysis.

Daily recomputation of constants used in the calculation equation is made possible by the time-sharing computer programs. New constants can be calculated in approximately six minutes in contrast to the more than 30 minutes formerly required using small office calculators.

The capability of the X-ray absorption method using the automated system in the analysis of samples is pointed out in Table 1. Analyses were performed in duplicate on two uranium

Table 1

STATISTICAL EVALUATION OF THE X-RAY ABSORPTION
ANALYSES OF URANIUM SAMPLES

Number of Samples ⁽¹⁾	Accepted Value (gm U/gm sample)	Mean Value by X-Ray Absorption (gm U/gm sample)	Standard Deviation of Duplicate Mean (gm U/gm sample)	Relative Standard Deviation (%)
11	0.005666	0.005683	± 0.000025	± 0.44
38	0.1150	0.1152	± 0.000364	± 0.32

(1) Analyzed in duplicate.

solutions, portions of which were sent to the laboratory over a period of three months without the foreknowledge of the analysts. The means of each set of duplicate results were used in the statistical computations.

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DETAILED INTERFACE LOGIC DIAGRAMS

Figure A-1. X-RAY ABSORPTION COMPUTER INTERFACE. (Logic Diagram)

Figure A-3. X-RAY ABSORPTION COMPUTER INTERFACE. (Power Schematic)

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