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HEAVY WATER ORGANIC COOLED REACTOR

DETERMINATION OF TOTAL OXYGEN IN $\text{Al-Al}_2\text{O}_3$ ALLOYS BY FAST NEUTRON ACTIVATION ANALYSIS

By
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ABSTRACT

A method for the determination of the oxygen content of Al-Al₂O₃ alloys, using fast neutron activation analysis, is described. Equipment with automatic control and techniques for improving the precision of measurements are specified. Over the range of 100- to 3000-mg oxygen, a precision of 1 to 3% (relative) is attainable, using dual sample irradiation with dual axis rotation during irradiation. The use of Lucite as an oxygen standard provides a stable, easily prepared reference material for the comparator technique used in activation analysis. Samples can be prepared, analyzed, and the data reported in much less than one hour per sample.

I. INTRODUCTION

Aluminum-alumina ($\text{Al-Al}_2\text{O}_3$) alloy is a dispersion-strengthened alloy which is being investigated for use as a nuclear-reactor fuel cladding. It generally is manufactured from aluminum powder which is either (1) covered with a natural oxide layer, (2) intentionally oxidized at a high temperature, or (3) blended with aluminum oxide (alumina) powder.^(1,2) The structural stability and mechanical properties of the alloy product (often designated SAP for sintered aluminum products) are related to the oxide content. Consequently, much effort has gone into the development of suitable analytical techniques for measuring oxide content.

Experience in this laboratory⁽³⁾ has indicated a lack of agreement among various analytical methods for determining oxide content (see Section III). The discrepancies arise probably through the indirect methods of determination used; i. e., aluminum is "separated" from the alloy, and that material which remains is considered as oxide. Because of these discrepancies a direct method was sought, and a program to develop fast-neutron activation analysis (FNAA) as the standard procedure to determine oxygen in aluminum-alumina alloy was inaugurated.

The activation-analysis method involves placing a sample in an environment which will make the element of interest radioactive (other elements may also become radioactive), then subsequently removing the sample from this environment and determining the disintegration rate of the activated element. The procedure is simplified and perhaps gives superior results if a comparator technique is used. Here one treats a standard sample (one that contains a known amount of the element of interest) and an "unknown" sample under identical conditions. A comparison of induced activities then yields the element abundance in the unknown sample through the relationship

$$W_{(\text{unk})} = W_{(\text{std})} \times \frac{A_{(\text{unk})}}{A_{(\text{std})}} \quad , \quad \dots (1)$$

where W is element weight, A is the induced radioactivity, and the subscripts unk and std refer to unknown and standard, respectively.

In FNAA for oxygen, radioactive ^{16}N , produced through the high energy (> 9.6 Mev), neutron-induced nuclear reaction on oxygen, $^{16}\text{O} (n, p) ^{16}\text{N}$, is determined by gamma scintillation counting.^(4, 5) The ^{16}N then gives a direct measurement of all oxygen in the sample, and thus should eliminate the shortcomings of other procedures applied to aluminum-alumina alloys. Only fluorine through the reaction $^{19}\text{F} (n, \alpha) ^{16}\text{N}$ directly interferes.

This report describes instrumentation, sample handling, and treatment of data for this analysis as it presently has developed over a 3-yr period in this laboratory. Many changes have been incorporated since beginning the program, and further refinements will undoubtedly be instituted in the future as the need for improvements occurs. It is hoped the experiences encountered to date will assist others and prevent some pitfalls.

II. EXPERIMENTAL

A. EQUIPMENT

The equipment utilized in developing this measurement technique was assembled from commercially available components. The activation analysis facility is comprised of a neutron source, a sample transfer system and its controls, gamma-ray detectors, and the associated electronics for performing gamma-ray spectrometry. Some of these items, illustrated in Figure 1, are described below.

1. Neutron Source

A Technical Measurement Corporation (TMC) Model 211 positive-ion accelerator was used to produce activating neutrons. Application and operation of such accelerators have been described in the literature.⁽⁶⁾

Accelerator targets are 1.25-in. -diameter discs of copper with titanium tritide (Ti^3H) deposited on one surface. (Targets used are purchased from U.S. Radium Corporation, Morristown, New Jersey.) Tritium concentrations of new targets are about 5 Ci/in.² The deuterons that strike the target induce the $^3\text{H}(\text{d}, \text{n})^4\text{He}$ nuclear reaction. The emitted neutrons have an energy of approximately 14 Mev. Neutron yield is roughly proportional to the amount of deuteron beam striking the tritium target. Maximizing this target current at any operating potential will generally give a greater neutron yield. Adequate neutron production with a new target will commence when the accelerating potential is increased to about 100 kv with a corresponding target current around 1 ma. As the target is "burned out" (several hours),⁽⁷⁾ however, operating potential must be increased until the maximum is reached at 200 kv. Although the 0- to 200-kv power supply current then measures about 5 ma, target currents only slightly above 2 ma are obtainable.

Because of irregularities in tritium distribution, fluctuations in the deuteron beam, and contaminants on the target surface, the neutron source cannot be considered as a uniformly-extended disc source. Figure 2 shows the image of the source (neutrons and x-rays) made on Polaroid film. This film was attached to the target surface and exposed for 300 sec. The "hot" spots will wander depending on accelerator operating conditions. Of course, at a long distance

Figure 1. Fast Neutron Activation Analysis Facility
(Neutron generator not shown)

Figure 2. Neutron Source Image

from the target, the neutron source may be considered a point source; however, since neutron flux is proportional to $1/(4\pi R^2)$, where R is the distance from the source, one prefers to place the sample to be activated as near the source as possible in order to induce the greatest activity.

2. Sample Transfer System

Since the ^{16}N activity resulting from oxygen irradiation has a half-life of only 7.35 sec, it is necessary to measure the radioactivity immediately following the irradiation. Moreover, the elapsed time between completion of the irradiation and beginning of counting must be accurately and reproducibly controlled. This almost certainly requires an automated transfer system.

Preliminary attempts at developing an automatic sample transfer system were unsatisfactory. The primary problems resulted from employing mechanical devices, e.g., mechanical relays, to control electronic functions. This gives "electronic" noise which can trigger scalers on or off, add spurious counts to scalers, or cause multichannel analyzers to "drop counts." Locating the source of this noise and trying to eliminate it are difficult and time-consuming. Similar problems were also encountered when a commercial unit was tested.

Figure 3. Sample Transfer System Flow Chart

An all-electronic, solid-state transfer control unit was ultimately developed which is precise, dependable, and compatible with nuclear instrumentation.* This unit was modified to control a TMC Model 168B sample transfer system which consists of polyethylene tubing, sample loading stations, routing gates, and irradiation and analyzing stations.

Samples are encapsulated for analysis in screw-on containers called "rabbits" made from high-density polyethylene 1 1/16-in. OD by 1-3/4-in. length and 1/2-in. ID, and 1/2 in. or 1 in. void length. Rapid sample transfer is achieved by pneumatically sending the rabbits through the polyethylene tubing.

The functions of the control unit are diagrammed in the flow chart shown in Figure 3. Upon pressing the start button, two timers are activated. One controls a burst of compressed gas, which blows rabbits through the polyethylene tubing to the neutron source. Compressed gas is obtained either from an argon gas-cylinder or from an air compressor-accumulator tank unit. The latter unit maintains a storage pressure of 120 lb/in.², and emits bursts of air that are adjustable up to the maximum pressure. Usually 80 lb/in.² bursts are adequate, and recovery to full pressure is rapid. Recovery has not caused delays in analysis. The gas cylinder is less desirable, since the gas is consumed in a short time (2 cylinders/wk were being used), and it is ultimately more expensive.

The second timer allows a time-lapse before irradiation commences. The time-delay is necessary to allow expanded gas to "bleed off" prior to starting the target-station sample rotator; otherwise, rabbits may be forced out of their rotating container and thus jam the rotation.

A modified TMC dual-axis, two-sample rotator is used to simultaneously irradiate two samples, whereas an in-house-built unit serves for one-sample rotation. The dual unit rotates rabbits simultaneously axially and radially in front of the target, so as to expose both rabbits to approximately the same irradiation environment. The closest source-to-rabbit distance is about 1.5 in. The single-axis unit rotates only axially and positions a rabbit about 0.5 in. from the source.

Rotation is necessary to insure uniform sample irradiation. As the devices rotate, a microswitch is tripped which causes a light to flash on the control unit.

*To be published by E. I. Ingham and E. T. Bramlitt.

This assures the operator that sample rotation is occurring. Factors which have prevented rotation include: bulged rabbits from too-tight caps, worn capsule surfaces, loss of caps during transfer, partial seating in the rotator because of an air cushion, restricted rotation mechanism (ball bearings, gears, etc). (Proper rabbit diameter is now checked before irradiation by slipping them through a brass gauge block.)

Timer 3 starts immediately when Timer 2 stops, and it (1) gives a pulse to start a scaler for flux monitoring, (2) provides voltage to initiate the irradiation rotator, and (3) provides a voltage to turn the irradiator on.

After adjusting the accelerator to desired steady conditions of high voltage, beam current, etc, which may take 20 to 30 min, there needs to be a way to terminate neutron production between irradiation cycles, primarily to conserve the Ti^3H target and reduce background. Three techniques commonly are employed for controlling neutron production: (1) deflect the deuteron beam off the Ti^3H target by means of an electromagnet, (2) insert a beam interrupter between the beam and Ti^3H target, (3) turn the ion source off. Approaches (1) and (2) have the disadvantage of permitting the deuteron beam to continue, so that eventually a deuterium target builds at the stopping location. It then is a source of 2.9-Mev neutrons produced through a $^2\text{H}(\text{d}, \text{n})^3\text{He}$ reaction, which can add to the background. The third technique is generally preferred.

The original TMC approach to (3) was to break the circuit to the ion-source (0 to 5 kv) power supply. Unfortunately, when the deuteron beam is then terminated, the main power supply (0 to 200 kv) will show an increase in operating potential, since its load has been removed. This increase is as much as 20 to 40 kv and if accelerator operation is near 200 kv, the permissible operating potential is exceeded and shutdown occurs. To avoid exceeding this limit, TMC installed a relay in series, and on the primary side of the Variac used to regulate the 0- to 5-kv transformer. When the ion source circuit was broken, this relay would short out part of the 0- to 200-kv Variac primary. A serious shortcoming of this approach is that inductive spikes occur on opening and closing the circuit. Arcing appears at relay contacts. Subsequent instrumentation is affected as previously noted.

A preferable solution developed is shown schematically in Figure 4. The ON-OFF switch (A/B) controls both the 0- to 5-kv Variac primary and a 115-v ac relay (Relay 1). When neutron generation is off, the 10Ω resistor reduces the 230-v ac supply to the 0- to 200-kv Variac primary; but when it is on, this resistor is shorted out to give full 230 v ac. The current changes in switching between ON and OFF are considerably less than are experienced when the Variac primary is tapped-off at different positions. The 20 to 40 v ac developed across the 10Ω resistor will not give the large induction arcs.

Further isolation of accelerator and analyzing instruments is achieved by using a mercury relay (Relay 2) in the automatic mode. The sample transfer system control unit operates this relay by means of SCR switches.

Irradiation terminates when Timer 3 (see Figure 3) stops; simultaneously (1) a pulse is generated which stops the flux monitor, (2) Timer 4 actuates the return gas force for a prescribed time, and (3) Timer 5 initiates a time-delay before analyzing begins. The delay provided by Timer 5 allows very short-lived activities to decay before measuring the activity of interest, and insures that both rabbits are at their respective analyzing stations. When Timer 5 stops, Timer 6 begins and it simultaneously gives pulses for starting scalers and analyzers, and gives voltage for sample rotators at the analyzing stations. These functions are terminated when Timer 6 stops. The control unit makes a decision whether to repeat the entire cycle or terminate.

Although not shown on the flow chart, all voltage supplies can be operated manually by means of switches, thereby bypassing the timer control.

3. Radiation Detection

Two radiation detection stations are used. One consists of two 5 x 5-in. NaI(Tl) crystals mounted face-to-face on Lucite supports. Each crystal is connected with a photomultiplier tube and preamplifier.⁽⁸⁾ Between the crystals is positioned a vertically-mounted, single-axis rotator. A 3/8-in.-thick, 7 x 7-in.-square aluminum block is attached to each side of the rotator to absorb high-energy beta particles. The entire detector assembly is centered in a 20 x 20 x 48-in. cave made of 4-in.-thick lead bricks lined internally with 0.1-in. cadmium and 0.25-in. aluminum sheet. Samples enter the rotator through a 1-in.-diameter hole in the lead top directly above the rotator. The second station is

NOTE: 0-5 kv ION SOURCE POWER SUPPLY
0-200 kv MAIN ACCELERATOR POWER SUPPLY

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Figure 4. Ion Source On-Off Circuit

identical with the first, except that it is smaller (20 x 20 x 20-in. inside dimensions) and has one 3 x 3-in. NaI(Tl) crystal adjacent to the aluminum absorber and rotator.

Regulated high voltage is provided for each photomultiplier tube by either John Fluke Co. Model 412A or TMC Model 520P units. Output pulses from each preamplifier are directed to the inputs of Cosmic Radiation Labs, Inc. Model 901 linear nonoverloading, double-delay-line clipped amplifiers. The amplifier prompt outputs are connected to Cosmic Radiation Labs, Inc. Model 901 SCA single channel analyzers (SCA). The dual-detector SCA outputs are passed through an OR gate and then, as is the single-detector unit SCA output, into Cosmic Radiation Labs, Inc. Model 1101-S nuclear scalers.

A TMC Model 404 multichannel analyzer (MCA) is used for setting the SCA windows. This is accomplished by routing the amplifier 2- μ sec delayed outputs into the independent inputs of the MCA. One hundred channels of memory are reserved for pulses entering each input. The SCA outputs (after proper shaping) are used to gate the MCA, so that each quadrant receives delayed amplifier pulses every time the corresponding SCA has an output; consequently the MCA scope display is of that portion of the sample gamma spectrum passed through the SCA window.

Neutron monitoring is accomplished with a Kaman Nuclear Corporation Model D-300 neutron dosimeter, which is essentially a neutron-sensitive (europium-activated Li^6I crystal) scintillator assembly in a 10-in. spherical polyethylene moderator. The pulse output is fed to a Cosmic scaler. Other detectors have been used, e.g., Nuclear Enterprises Model NE 404 plastic scintillator with photomultiplier. In this case, the amplifier pulses were sent to an SCA for discriminating low-energy neutrons before scaling.

B. ANALYSIS PROCEDURE

1. Sample Preparation

Samples of aluminum-alumina alloy bar stock and rod are machined to fill the internal volume of a rabbit. A number of finned-tubing alloy samples have been analyzed. These are cut to the necessary length and then flattened by pressing in a vise. The material breaks rather easily into strips which can

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Figure 5. Typical ^{16}N Decay Curve

then be placed in a rabbit to fill most of its volume. Residual air does not contribute a significant error to the measurement in the concentration ranges studied.

Standards have been made from sufficient tartaric, oxalic, and benzoic acids or Lucite to fill a rabbit. In some cases, reactor-grade graphite has been intimately mixed with various weights of either Al_2O_3 or SiO_2 and then packed into a rabbit to serve as standards.

2. Activation

Two approaches to activation analysis were studied, viz, sequential and simultaneous irradiation of standard and "unknown" samples. In the sequential method, one rabbit at a time is activated and analyzed. The single-sample transfer system is used. Irradiate, count, and transfer times are maintained constant, and corrections in flux variations from one irradiation to the next are made by monitoring the integrated neutron dose and determining sample activity/neutron count. Radioactive measurements are performed using the dual-detector station. In the simultaneous method, both standard and "unknown" samples are processed at the same time by using the two-sample transfer system. The unknown is counted in the dual-detector station while the standard is counted in the single-detector station.

3. Radioactive Counting

The SCA windows are adjusted to detect the ^{16}N full-energy gamma peaks in the 5- to 7-Mev region. The SCA base lines are increased until no ^{24}Na 4.75-Mev gammas from $^{27}\text{Al} (n, \alpha) ^{24}\text{Na}$ are detected. Background counts are made routinely on samples as a check on possible buildup of long-lived interfering activities. Occasionally the SCA outputs are fed to the MCA operated in the multiscale mode with 1 sec/channel, so that the activity decay can be used to confirm that only ^{16}N is counted. Figure 5 shows a typical decay curve. Straight lines even at high count rates confirm that no losses result from equipment dead-time. When the simultaneous sample treatment is used, no neutron monitoring is required, but it is necessary to determine the relative efficiency for the two counting stations. This is accomplished by irradiating two identical Lucite standards and comparing activities to get a "detector ratio."

A calibration line of activity vs added oxygen was generally used to determine unknown oxygen content when the sequential method was employed. For the simultaneous method, determinations are made relative to one standard only. At least three determinations are made on each aluminum-alumina alloy sample analyzed. The average oxygen content is then multiplied by 2.125 (alumina/oxygen gravimetric factor) to express it as Al_2O_3 . A standard deviation for a single analysis is computed.

Most analyses were performed with irradiation times around 21 to 30 sec, transfer delay times 2, 3, or 4 sec, and analyzing times of 24 or 30 sec.

III. RESULTS AND DISCUSSION

Standards of the different materials with oxygen content ranging from 23 mg to 3.7 gm have been analyzed to obtain calibration lines of measured activity vs added oxygen. Data points fell very close to a straight line, confirming the value selected for each standard. Since reuse of the powder standards may cause compaction that would introduce geometry errors, solid Lucite was selected as the preferred standard. It is assumed to be an acrylic resin that contains 32% oxygen by weight. Confirmation of this abundance was obtained by comparison with the organic acids. These results are shown in Table 1.

TABLE 1
DETERMINATION OF OXYGEN IN LUCITE

Sample	Weight Lucite (g)	Theoretical Oxygen (g)	Experimental Oxygen (g)
1	3.8773	1.243	1.248 $\pm$ 0.006
2	3.9666	1.269	1.269 $\pm$ 0.009
3	3.8766	1.241	1.244 $\pm$ 0.008

Since most aluminum-alumina alloy samples analyzed contain over 500 mg oxygen, any error resulting from oxygen impurity in the polyethylene rabbits should be insignificant. Fourteen randomly-selected rabbits were analyzed for oxygen. The average blank value was 2.1 mg with a 9.5% relative standard deviation for a single analysis, and 2.5% relative standard deviation of the mean.

The error introduced by samples not completely filling the 1/2 x 1-in. rabbit was found to be small. This was determined by analyzing various weights of tartaric acid and using an oxygen gravimetric factor of 0.64. These results are given in Table 2. The discrepancies are probably due to a change in geometry of the powder samples due to compaction. The small void in the finned-tubing samples is not expected to give as large an error as observed in the powder.

Sample rotation improves precision. This is demonstrated by repeated measurements made on a single sample. A standard deviation of 15% when

Figure 6. Variation of Count Rate

TABLE 2
DETERMINATION OF OXYGEN IN TARTARIC ACID

Sample	Tartaric Acid (mg)	Theoretical Oxygen (mg)	Experimental Oxygen (mg)	Theoretical - Experimental	
				(mg)	(% Theoretical)
1	219.2	140.3	136	-4	-2.8
2	1172.2	750.2	742.2	+8	+0.11
3	490.0	313.6	307	+6.6	+2.1
4	97.0	62.1	58.5	+3.6	+5.8
5	2237.0	1431.7	1477	-45	-3.1
6	1671.0	1069.4	1087	-18	-1.7
7	3682.1	2356.5	2382	-25	-1.1
8	3682.2	2356.6	2373	-16	-0.7

sample rotation was not used and 2.9% when sample rotation was used is observed.

Simultaneous sample treatment is preferred to sequential treatment. Although satisfactory determinations can be made by the latter method, precision is strictly dependent on neutron generation being steady and uniform. This is not always possible. Often the accelerator does not operate smoothly. This is especially the case when it has not been utilized for several days. The beam current will drift and fluctuate even during a short irradiation. These effects are evidenced in Figure 6. These curves were obtained for repeat irradiations of two equivalent Lucite standards. Plotted are consecutive integrated counts (N) obtained from the neutron monitor, the ratio of dual-detector to single-detector counts ($5 \times 5 / 3 \times 3$), the ratio of dual-detector counts to neutron counts ($5 \times 5 / N$), and the ratio of single-detector counts to neutron counts ($3 \times 3 / N$). The precision is obviously superior when the detector ratios are used, corresponding to a simultaneous determination approach. The standard deviations for the first 30 irradiations are 11.4% for the dual-detector station, 11.8% for single-detector station, and 4.2% for the ratio of these two.

Detector-system stability is shown in Figure 7, which is a plot of frequency of occurrence for detector ratios measured during an operating day. The average detector ratio for 79 determinations is 2.49 ± 0.42 , corresponding to a

Figure 7. Frequency of Occurrence for Detector Ratios Measured During One Day

standard deviation of 1.70% and a standard deviation of the mean of 0.19%. A computed Gaussian-distribution curve has been traced over the data points.

Long-term stability is indicated by the data collected over a 12-calendar-day period and presented in Table 3. The ratios were obtained for the two rabbit sizes utilized. During another 11-day period, a drift of only 0.13% was noticed. Since system drift is negligible, it is sufficient to verify the ratio, rather than exhaustively calculate it during each experimental run, provided the same instrument settings are used.

TABLE 3
DETECTOR RATIOS

Measurement (day)	1/2 x 1/2-in. Sample	1/2 x 1-in. Sample
1st	2.26 $\pm$ 0.083	2.22 $\pm$ 0.051
2nd	2.24 $\pm$ 0.091	2.20 $\pm$ 0.045
3rd	-	2.21 $\pm$ 0.060
10th	2.27 $\pm$ 0.13	2.23 $\pm$ 0.045
11th	-	2.25 $\pm$ 0.067
12th	2.29 $\pm$ 0.14	-

Early work on the comparison of oxygen determinations using FNAA and anhydrous hydrogen chloride gave data tabulated in Table 4.⁽³⁾ For some formulations agreement is very good, but often unexplained discrepancies exist. In an attempt to validate the accuracy of the FNAA method, i. e., demonstrate the absence of a bias, an interchange of samples and reference standards with Oak Ridge National Laboratory (ORNL) was accomplished. The absolute oxygen content of two Atomics International (AI) reference standards was determined by using ORNL-prepared standards as a base. Comparison showed agreement within 3% (relative). Three tubing samples which had been previously analyzed at AI were analyzed at ORNL, first by FNAA, then by an improved anhydrous hydrogen chloride method. Comparative results are shown in Table 5.

TABLE 4
ANALYSIS OF ALUMINUM-ALUMINA
ALLOY FOR Al_2O_3

Sample	FNAA Method (wt %)	HCl Method (wt %)
1	6.75 ± 0.31	7.02
2	6.90 ± 0.22	6.96
3	6.90 ± 0.59	7.11 ± 0.22
4	6.88 ± 0.50	6.89 ± 0.07
5	7.13 ± 0.41	6.86 ± 0.07
6	7.13 ± 0.23	7.75 ± 0.18
7	7.06 ± 0.05	7.90 ± 0.12
8	6.97 ± 0.35	7.81
9	6.77 ± 0.32	7.77
10	9.27 ± 0.32	10.22
11	9.05 ± 0.16	10.03
12	9.39 ± 0.09	10.29
13	9.40 ± 0.10	10.18
14	9.42 ± 0.13	10.24
15	9.24 ± 0.18	10.32

TABLE V
INTER-LABORATORY AND METHOD COMPARISON

Sample Number	AI* (FNAA) (wt %)	ORNL (FNAA) (wt %)	ORNL (Anhyd HCl) (wt %)
B3-1	10.50 ± 0.36	10.45 ± 0.23	10.62 ± 0.04
B4-1	10.61 ± 0.34	10.40 ± 0.25	10.26 ± 0.41
B4-2	10.43 ± 0.29	10.50 ± 0.32	10.20 ± 0.27

*Uncertainties represent one standard deviation. AI's data were accumulated prior to installation of dual transfer system and do not represent best possible precision.

Any bias caused by surface oxidation while preparing samples is minimal. One sample of alloy 1/2 in. x 1 in. was analyzed and found to contain $6.58 \pm 0.10\%$ Al_2O_3 . It was then sectioned into eight discs (about 1/2 in. x 1/8 in.), and analyzed as one sample. The result was $6.42 \pm 0.14\%$ Al_2O_3 , in essential agreement with the first determination.

A complete report on evaluation of results by this FNAA method is reported.⁽⁹⁾

There was no evidence in the observed gamma-ray spectra of the presence of fluorine which, if present, could have caused a bias in the measurement as mentioned earlier. The presence of fluorine is ascertained by searching for the 0.51-Mev annihilation peak from 10-min ^{18}F arising from $^{19}\text{F}(\text{n}, 2\text{n})^{18}\text{F}$. The absence of such a peak gives evidence of the absence of fluorine. If it were present, it is in such low concentrations as not to influence the oxygen measurement.

IV. CONCLUSIONS

Earlier differences (Table 4) between results obtained by the anhydrous hydrogen chloride and FNAA methods have been resolved in favor of the FNAA Method (Table 5). When a sample of the Al-Al₂O₃ alloy is heated in vacuum at 600°C for 40 hr, comparable results are obtained by FNAA, anhydrous, and aqueous HCl methods.⁽¹⁰⁾ The presence of β -Al₂O₃ · 3H₂O in the alloy could account for low results using aqueous HCl and for high results using anhydrous HCl. The hydrated oxide is soluble in hot acid solution giving rise to losses of the oxide and a negative bias. In the anhydrous method, formation of AlCl₃ · 6H₂O, which would not volatilize, would give rise to higher "oxide residue" values and a positive bias. The 600°C treatment destroys the hydrated species yielding an acid insoluble Al₂O₃ and removing the water thereby precluding the possibility of formation of the hydrated chloride. By interlaboratory comparison, accuracy of the determination is within ± 3%. Over the range of 100 to 3000 mg oxygen, a precision of 1 to 3% relative standard deviation has been attained.

In one month's operation, 361 determinations of percent Al₂O₃ in aluminum-alumina alloys were completed. The wet chemical (anhydrous hydrogen chloride) method would have required about 270 man-days for this work. FNAA accomplished it in 72 man-hr, or less than 15 min/determination, including sample preparation, analysis, and reporting. This corresponds to a time reduction of greater than 90%.

The FNAA dual-sample (simultaneous) procedure using Lucite standards should be considered a preferred method for determining oxygen content of aluminum-alumina alloys because of its excellent precision and accuracy, as well as the rapidity with which analyses can be completed.

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