

## A Critical Review on the Determination of Aluminum Metal.

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### <Abstract>

The analytical methods of aluminum metal are reviewed for about 2 decades up to 1970.

Prior to the past two decades few accurate quantitative methods were recorded for the determination of micro amount of aluminum.

Volumetric methods were widely used particularly for this aluminum metal. Colorimetric, spectrofluorometric, X-ray fluorescence, spectrographic, and gravimetric methods are also applied in industrial purposes. Generally it is a fact that coincident with a improvement in the economic status of a metal, there is a corresponding impetus in the development of methods for its analytical determination. Along with the great improvement in the economics of the aluminum metals and its alloys are found a really significant advance in the recorded analytical methods for aluminum in various matrices. Recently the nuclear chemical techniques may be considered very powerful tools for an accurate determination of submicrogram amount of aluminum in high purity materials or in alloys. The past two decades have seen a rapid increase in the number of effective analytical methods of separation and determination.

Despite of the accumulation of the data, it seems to be very hard to manage for their routine work in an industry because of their lackness of new knowledge of nuclear and radiochemistry in the developing country like Korea.

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### 알미늄 분석법

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### <요 약>

필자는 1970년 이전의 약 20년간에 보고 되었던 알미늄 금속의 분석법에 관한 논문들을 다시 검토해 보았다. 1970년대 이전에 발표된 문헌들로 미루어 보아 그 당시에는 미량 성분의 알미늄 금속 분석에 관한 연구가 그다지 활발하지 못했다 하겠다. 그러나 필자가 조사한 기간에는 미량 성분의 분석에 관한 연구가 괄목할 만큼 두드러지게 나타났으며 용량 분석방법이 특히 많이 쓰였음을 엿볼수 있었다. 기타 중량법과 흡광 분광 광도법, 분광 형광 분석법, 발광 분광 광도법, 방사화 분석법 등등의 기기분석 방법이 공업적으로 점차 많이 쓰였음을 알수 있었다.

분석 방법은 금속의 경제적인 이용도가 개발됨에 따라 실지로 현저하게 발전되었음을 보고된 문헌을 통

하여 알수 있다. 요즈음에는 핵화학에 관한 기술이 고 순도 물질이나 합금들에 들어 있는 극미량의 알미늄을 정확하게 정량하는 극히 좋은 수단이 되고 있는것 같다.

지난 20년간에 좋은 방사 화학적인 분석법과 분리 방법이 급증 하였지만 우리 나라 공업계에서는 아직도 이에 관한 새로운 기술의 결핍으로 공정의 제품 관리에 사용되고 있지 않다.

### I. Spectrofluorometric methods

To determine traces of aluminum of the order of 2 ppb levels, a double monochromator spectrofluorometer which fitted with a 150-watt Xenon arc lamp and RCA IP 28 multiplier phototube, and equipped with a Honeywell brown recorder was used by Kirkbright, G. F. et al(17). The fluorescence intensity of the blue fluorescent aluminum complex of 2-hydroxy-3 naphthoic acid was measured at 460  $m\mu$  and at pH 5.8. The precision of the fluorescence intensity measurements for aluminum was  $\pm 2.0\%$ , corresponding to  $\pm 0.05\mu\text{g}$  of aluminum. The following ions were not interfere when present in 1000 fold molar excess over the 10g of aluminum present in 100ml of aqueous solution: Ag, Li, Na, K,  $\text{NH}_4^+$ , Mg, Ca, Sr, Ba, Co (II), Ni, Fe (II), Mn(II), Pb, Cd, Hg(II), As(III), Ce (III), V(V),  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{CN}^-$ ,  $\text{NO}_3^-$ ,  $\text{ClO}_4^-$ ,  $\text{SCN}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ , and  $\text{S}_2\text{O}_3^{2-}$ . NO Fe (III) could be tolerated, but its interference at the 1000-fold excess level can be reduced to approximately -10%, although it could not be eliminated quantitatively by reduction to Fe(II) with the required amount of ascorbic acid in the absence of chloride ion. The solution including chloride absorbs at the wavelength of excitation, and reduces the intensity of the fluorescence.

A method for determining micro amounts of aluminum was described by Noll, C. A. et al (12) for a fluorometric and spectrophotometric determination. The aluminum was complexed with fluoride to prevent its reaction with 8-

quinolinol while interfering ions are removed by exposing them to a weak cationic ion exchange resin (IRC-50 R.G.) and the aluminum was then made reactive to the 8-quinolinol and its chloroform-extracted 8-quinolinate was measured by Baush & Lomb Spectronic 20, maximum absorbance was found to be at 380  $m\mu$ . The range of the test was from 0.00 to 0.50 p.p.m. as aluminum with a standard deviation of  $\pm 0.02$ .

### II. Spectrophotometric methods

Villarreal, R. et al (16) reported a highly selective method for the separation and determination of aluminum by spectrophotometer. The procedure was based on the extraction of aluminum with N-benzoyl-N-phenylhydroxylamine (BPHA) into benzene from an ammonium carbonate solution containing several masking agents(i.e. thioglycolic acid(TGA), potassium cyanide, sodium hexametaphosphate and hydrogen peroxide). Aluminum was back-extracted into 0.20 M HCl, complexed with 8-quinolinol and the colored complex extracted into chloroform and measured at 390  $m\mu$ .

One hundred and fifty mg. of  $\text{U}^{+6}$  did not interfere in the method. Ten mg each of  $\text{Ni}^{+2}$ ,  $\text{Sb}^{+5}$ , Sr,  $\text{Cr}^{+6}$ ,  $\text{Mo}^{+6}$ , Na, Th, Li,  $\text{Fe}^{+3}$ , K,  $\text{Pb}^{+2}$ , Mg, Cs, one mg each of In, Be, Cd,  $\text{Sn}^{+4}$ ,  $\text{Mn}^{+7}$ , Rh,  $\text{Ru}^{+3}$ , Zr,  $\text{Pt}^{+4}$ , Ba, La, Y, Pd,  $\text{Ce}^{+4}$ , Ca,  $\text{Co}^{+2}$ ,  $\text{V}^{+5}$ ,  $\text{Re}^{+7}$ , Zn,  $\text{Cu}^{+2}$ ,  $\text{Nb}^{+5}$ ,  $\text{Bi}^{+3}$ , mixed-rare-earth elements, 0.5mg Ga, up to 100mg of formate, acetate, oxalate,

borate, phosphate, perchlorate, nitrate, sulfate, cyanide, bromide, iodide, and triethanolamine, and 50mg of tartrate, gave no interference in the method. Beer's law was obeyed up to 50 $\mu$ g aluminum in 10ml of chloroform.

The optimum range was 5-30 $\mu$ g aluminum. For the determination of aluminum at the 0.01% level in uranium alloy and the 0.05% level in stainless steel, the relative precision of the method at the 2 $\sigma$  level was  $\pm 2\%$ .

Eriochrome Cyanine R reagent was used by Študlar, K. et al (1) for the photometric determination of aluminum in steels. A nitrated Eriochrome cyanine R reagent had been used in a procedure involving removal of iron and many interfering ions by a hydroxide precipitation with the addition of metallic zinc which concurrently reduces chromium and vanadium and thus required the subsequent removal of vanadium(IV) by 8 quinolinol into a halocarbon. The authors stated that this procedure yields satisfactory results with simple steels, and also with chromium-nickel, chromium-vanadium, chromium-tungsten-vanadium, and even high-alloy steels.

Poetzl (18) used a differential technique for accurate photometric analysis of high concentrations of aluminum. He stated that precipitation or complexometric reactions can be used to remove an accurately defined portion of ions to be determined so that low residual concentration can be determined with high relative accuracy. Aluminum can be determined after partial masking with EDTA and complex formation with ferron. Concentration of the later is determined photometrically. Results compare well with those of other methods.

Qureshi et al (19) used paper chromatography to separate aluminum, titanium, and iron quantitatively from each other. Solvent systems reported were 3 : 5 : 2 and 3 : 4 : 3 HCO<sub>2</sub>H-HCl-Me<sub>2</sub>CO, respectively. Aluminum was determined photometrically with thiochrome cyanine R, titanium with sulfosalicylic acid at 410 m $\mu$  and iron with 1, 10-phenanthroline. Results of se-

parations and determinations on synthetic solutions were presented.

Culp (20) in determining aluminum in an aluminum-titanium binary alloy used lactic acid to mask the titanium while backtitrating an excess of EDTA with bismuth. The indicator was Xylenol Orange at pH 5.0 to 5.5.

A new reagent, 5-sulfo-4'-diethyl amino-2'-2-dihydroxyazobenzene (DDB), was proposed by Florence, T.M. (2) for the spectrophotometric determination of aluminum in the presence of beryllium. At pH 4.7 and 540 m $\mu$ , the aluminum-DDB complex has a practical molar absorptivity of 41,000, corresponding to 0.00066  $\mu$ g per sq cm on the Sandell scale. Large amounts of beryllium depress the aluminum color. Most interfering metals could be masked with (ethylene dinitrilo) tetraacetic acid (EDTA) or ferrocyanide, while gross amounts of impurities might be removed by a rapid triisooctylamine extraction from 8 M hydrochloric acid.

The test was carried out on 6 $\mu$ g of aluminum, using his procedure with a relative standard deviation of  $\pm 0.5\%$ . The formation of the aluminum-DDB complex was sufficient to develop maximum color at 40°C, but higher temperatures did not affect the sensitivity.

Certain di-O-hydroxyazo compounds -i.e., Superchrom Garnet Y(5-sulfo-2'4'2-trihydroxyazobenzene)-was known to form strong complexes with aluminum, but not with beryllium (21), and had been used for the polarographic determination of aluminum in beryllium (22) and thorium compounds(23).

Another well known method of the colorimetric determination of aluminum which described by Lundell et al (37, 38) is the formation of a red lake with Aurin tricarboxylic acid, to which dye the trival name aluminon has been given.

The colorimetric determination of less than 0.1mg of aluminum by means of aluminon is very satisfactory when no interfering ion is present, but there are so many possibilities of interference that anomalous results are often

obtained.

A similar lake is formed with beryllium. Iron, the chief interfering element, must be absent because small quantities of iron give a purplish red tint. Large quantities of phosphate prevent the formation of the aluminum lake. Silicon, bismuth, lead, antimony, mercury, and titanium give white precipitates. Large quantities of alkaline earths, basic salts, or hydroxides of chromium, yttrium, lanthanum, cerium, neodymium, erbium, zirconium, scandium, or thorium give red lakes. But, fortunately, these are either dissolved or decolorized by ammonium carbonate. Cadmium, zinc, manganese, nickel, and cobalt give no precipitate.

Bensch (87) applied Alkalone I (dihydroxytartaric acid 2, 4-dinitrophenylosazone) to the determination of free hydroxide and aluminum in sodium aluminate solutions by a recording photometric titration.

A potentiometric method was developed by Watts and Utley (88) in which the free alkali and that bound in the sodium aluminate, as well as the sodium carbonate, is titrated with HCl in the presence of sodium gluconate as a complex former.

The aluminum content is determined by titration of the hydroxyl ions set free by reaction with potassium fluoride.

Danchik, R.S. et al (85) proposed the direct determination method of hydroxide and the indirect determination method of aluminum in sodium aluminate solutions. A semi-automatic system was developed to determine hydroxide concentration by direct spectrophotometry.

A 1:10 diluted sample of sodium aluminate solution is mixed with a  $7\frac{1}{2}\%$  sodium gluconate- $1\frac{1}{2}\%$  sodium carbonate mixture causing hydroxyl ion to be released from the aluminum gluconate-hydroxide complex. Air is introduced in increments and segregates the sample mixture into fractional milliliter portions. These small

segmented portions are mixed for a period of approximately 1 min. while passing through a coil. After the mixing step, an aliquot is removed and the bubbles and excess solutions are directed to waste. The aliquot is mixed with the Alkalone I solution, again segmented with air, and proceeds through a second mixing coil and a time delay coil. A second debbling and aliquot step take place and a continual stream of reacted mixture flow through the sampling cell in the spectrometer and a reading in absorbance is obtained at  $550m\mu$ . The total elapsed time for passage of the sample through the system is 10 minutes. A standard deviation on a standard solution of 0.26N sodium hydroxide was 0.002 absorbance unit.

Colorimetric method for the determination of aluminum was investigated by Zibulsky, H. et al (6). This rapid and accurate procedure was proper for the determination of about 0.01 to 6% aluminum in steels and heat-resistant alloys. The method made use of the fact that a cupferron-chloroform separation followed by complexing agents enables a satisfactory color extraction of aluminum with 8-quinolinol in chloroform.

Measured the absorbance of solution at either 380 or 425  $\mu$  against a blank containing all reagents with no aluminum.

The reaction of 2-quinizarin sulfonic acid (sodium salt) with aluminum ions in methanol to give a stable violet complex had been applied to spectrophotometric determination of aluminum by Owens II. E. G., et al (4). This method had been successfully applied to several bronze and steel samples after preliminary separation of interfering ions from aluminum with the mercury cathode. Interfering ions not thus removed were:  $Be^{+2}$ ,  $Sc^{+3}$ ,  $Th^{+4}$ ,  $Ti^{+4}$ ,  $Y^{+3}$ ,  $Zr^{+4}$ ,  $F^{-1}$ ,  $Po_4^{-3}$ , and the rare earths. Optimum concentration of aluminum in bronze or steel was from 0.01 to 1.0%. The reaction had a spectrophot-

ometric sensitivity of 1 part of aluminum in 50,000,000 parts of solution. The spot plate sensitivity was 0.25 $\gamma$ , with a concentration limit of 1 to 200,000; spot paper sensitivity was 0.5 $\gamma$ , the concentration limit being 1 to 100,000. Maximum wavelength of absorbance for the violet complex was at 560 m $\mu$  and Beer's law was obeyed up to an aluminum concentration of 1.7 ppm.

The reagent, 1,4-dihydroxy-2-anthraquinone sulfonic acid (2-quinizarinsulfonic acid), had been investigated in the colorimetric determination of beryllium in aqueous medium (24) and in the fluorometric determination of beryllium (25).

A large number of metals could be conveniently separated from aluminum in one step by electrolysis at the mercury cathode. Scherrer and Mogerman (26) used this method for separation of interfering ions prior to determination of aluminum with aluminon.

### III. Emission spectrographic methods

For the determination of 5-40 $\gamma$  of aluminum, Eshelman, H. C. et al (7) used flame spectrophotometric method. They could be selectively extracted the aluminum from an acetate-buffered solution adjusted to pH 5.5 to 6.0 with a 0.1M solution of 2-thenoyltrifluoroacetone in 4-methyl 2- pentanone; or from an acetate-buffered solution adjusted between pH 2.5 and 4.5, and containing N-nitrosophenylhydroxylamine(Cupferron), with 4-methyl-2-pentanone. The organic phase was aspirated directly into an oxyacetylene or an oxyhydrogen flame and the emissivity of aluminum was measured at either the atomic line at 396.2 m $\mu$  or the sharp oxide band head at 484m $\mu$ . When a 4-methyl-2-pentanone rather than an aqueous solution of aluminum, was aspirated into the flame, the emissivity was increased 100-fold. At a slit width of 0.030 mm, the sensitivity was 0.5 $\gamma$

of aluminum per ml per scale division (% T). The effect of a large number of interferences on the emission intensity of aluminum was shown in table I.

Except for a brief reference to the emission of aluminum in an oxycyanogen flame (27), only several indirect methods (28. 29. 30. 31) for the determination of aluminum have been reported, based on the depressant effect of aluminum upon the flame emission of calcium.

A method for the quantitative spectrographic determination of aluminum was used a powder-pellet spark technique by Veleker, T. J. et al(9).

This spectrographic method offers a rapid, precise control of aluminum in one of the manufacturing steps of tungsten wire and rod for the electrical industry. The spectral lines, analytical range, and precision of the determinations are listed in Table II (32). The reproducibility of the methods was expressed as the coefficient of variation.

Typical spectrographic results on standard I of aluminum were 0.042, 0.040, 0.044, 0.038, 0.040, 0.040 and 0.040%, respectively.

Table I. Tolerance limits for diverse ions (aqueous phase contained 200 $\gamma$  of aluminum; 10ml of 4-methyl-2-pentanone used as extractant)

Diverse ion present	Tolerance limit, mg., for chelating agent	
	2-thenoyl trifluoroacetone	N-Nitrosophenylhydroxylamine.
Barium	10	50 <sup>a</sup>
Boron	2	25
Cadmium	10 <sup>a</sup>	5
Calcium	50 <sup>a</sup>	50 <sup>a</sup>
Cerium(III)	1	5
Chromium(III)	0.2	10
Chromium(V)	20 <sup>a</sup>	0.5
Cobalt	1	0.5
Copper	1	0.5
Iron(III)	2	2

Lanthanum	10 <sup>a</sup>	10 <sup>a</sup>
Lead	—	10 <sup>a</sup>
Lithium	2	10 <sup>a</sup>
Megnesium	10	50 <sup>a</sup>
Manganese	0.5	50
Molybdenum	0.25	1
Nickel	0.2	5
Potassium	10	10
Sodium	50 <sup>a</sup>	50 <sup>a</sup>
Strontium	—	50 <sup>a</sup>
Thorium	10	10
Titanium	4	1
Uranium	10	10
Vanadium	—	10
Yttrium	—	0.1
Zinc	10	10
Chloride	100	100 <sup>a</sup>
Fluoride	0.2	0.2
Nitrate	50 <sup>a</sup>	50 <sup>a</sup>
Perchlorate	100 <sup>a</sup>	100 <sup>a</sup>
Phosphate	0.2	0.2
Silicate	—	50 <sup>a</sup>
Sulfate	100 <sup>a</sup>	100 <sup>a</sup>

a: Maximum quantity tested

Table II. Spectral lines, Range, and precision

Element line, A.	Internal Std. line, A.	Range, %	Precision, %
Al 3092.713	W 3092.285	0.005-0.15	7

<sup>a</sup>Precision is expressed as the coefficient of variation,  $v$ , and is calculated as follows:

$$v = \frac{100}{C} \sqrt{\frac{\sum d^2}{n-1}} \quad \text{Where } C = \text{av. concn., per cent}$$

$d$  = difference of detn. from the mean  
 $n$  = No. of detns.

### III. Potentiometric methods

A Potentiometric titration method was used to determine aluminum remotely by Baumann, E. W. (90) using a technique similar to that for determination of Lithium (91). The aluminum is titrated with fluoride in ethanol using a

lanthanum fluoride electrode(92). In the presence of sodium ion, insoluble cryolite ( $\text{Na}_3\text{AlF}_6$ ) or a similar compound is formed. The ratio of six fluorides to one aluminum favors determination of small quantities of aluminum.

A typical potentiometric titration curve is shown in Figure 1.

The potential change at the equivalence point is 20mv for a  $20\mu\text{l}$  addition of 0.1M NaF. The relative standard deviation is 1 to 2% for the method at 10 micromoles of Al(III). The presence of radioactivity does not affect the fluoride titration. Successful potentiometric titration of aluminum with fluoride depends upon removal of other ions that form complexes or insoluble compounds with fluoride. The method is based on the postulated formation of an aluminum hexafluoride that is insoluble or undissociated in ethanol.

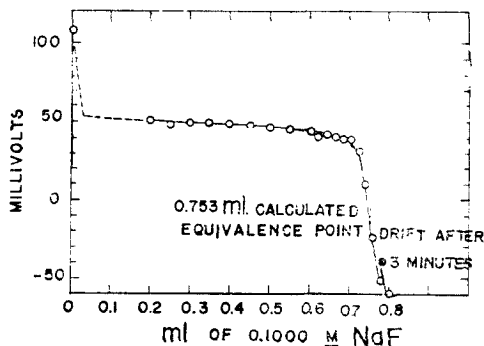


Fig. 1. Curve for titration of aluminum with fluoride in ethanol (solution: 50  $\mu\text{l}$  of 0.25 M  $\text{Al}(\text{NO}_3)_3$ , 0.5ml of 1 M NaOH, 0.5 ml of 1 M  $\text{HNO}_3$ , 15 ml of ethanol, 1 ml of pH 5 buffer)

### V. Gravimetric methods

Pender, H. W. (5) reported that a rapid, gravimetric method for the quantitative determination of aluminum in titanium and other alloys in the range of 1 to 10% was applicable without preliminary chemical separation to alloys

containing such elements as manganese, vanadium, tin, lead, zirconium chromium, iron copper and molybdenum. Samples were dissolved in dilute hydrofluoric acid and oxidized with hydrogen peroxide. The aluminum was precipitated with a solution of sodium fluoride and the sodium fluoaluminate formed was removed by centrifugation. The sodium fluoaluminate or double salt was then reprecipitated. The solution was centrifuged again, and the double salt was washed with dilute sodium fluoride solution, dried and weighed as  $11 \text{ NaF} \cdot 4\text{AlF}_3$ .

The Author said that this method required approximately one half the time and effort needed by other methods of chemical analysis and gives the required accuracy and precision.

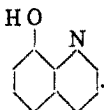
To determine aluminum as oxide, it is precipitated as the hydrated oxide which, as Bemmen V. (33) has shown, is really  $\text{Al}_2\text{O}_3 \cdot \text{XH}_2\text{O}$  rather than the hypothetical  $\text{Al}(\text{OH})_3$ . The hydrated oxide is amphoteric and tends to form colloidal solutions.

Because of its amphoteric nature it is best precipitated, as Blum (35) has shown, by keeping the hydrogen-ion concentration at about  $10^{-7}$ , as it is in pure water. Owing to the colloidal nature of the precipitate it is advisable to have ammonium salt in the solution and to wash the precipitate with water containing ammonium salt. The ammonium salt also prevents the precipitation of magnesium hydroxide by repressing the ionization of ammonium hydroxide. Since  $\text{Al}_2\text{O}_3$  is hygroscopic and difficult to weigh unless it has been heated above  $1100^\circ\text{C}$ , it is best to finish the ignition in an electric furnace which is heated to  $1200^\circ\text{C}$ .

According to Britton(34), aluminum hydroxide begins to precipitate at  $\text{pH}=4.14$  and the precipitate is dissolved at  $\text{pH}=10.8$ . Most separations of aluminum from other metal ions are based upon the regulation of the  $\text{pH}$  by use of ammonium hydroxide and ammonium chloride.

Lundell and Knowles (36) have shown that the determination of small quantities of aluminum as phosphate can give very accurate and reproducible results.

8-hydroxyquinoline also apply to gravimetric determination of aluminum(39). 8-Hydroxyquinoline, for which the trival name oxine has been proposed, has the empirical formula  $\text{HO} \cdot \text{C}_9\text{H}_6\text{N}$  and the structural formula

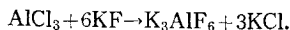


The hydrogen of the OH group is replaceable by metal, and precipitates are produced under suitable conditions when the reagent is added to solutions containing ions of magnesium, aluminum, copper, bismuth, cadmium, zinc, mercury, lead, antimony, tin, vanadium, iron, titanium, tantalum, columbium, manganese, nickel, or cobalt. The reagent, therefore, is not specific for any particular ion, but the solubility of the various precipitates varies enough so that it can be used for numerous separations. None of the precipitates are formed strongly acid solutions. The precipitate,  $\text{Al}(\text{C}_9\text{H}_6\text{ON})_3$  is easier to filter than aluminum hydroxide or phosphate, and some useful separations of aluminum from other elements can be accomplished with this organic reagent. The precipitate can also be dissolved and the 8-hydroxyquinoline determined volumetrically.

## VI. Volumetric methods

Scott (40) in a modification of Craig's (41) method, described a procedure for determining aluminum in which two portions of the sample are titrated. One aliquot of the solution of aluminum in excess free acid is titrated with sodium hydroxide to the phenolphthalein end point. This results in neutralization of the excess free acid and precipitation of aluminum

as the hydroxide and permits calculation of the total acid content of the solution. Another aliquot of equal size is treated with an excess of potassium fluoride to precipitate potassium cryolite.



Subsequent titration of the resulting suspension with sodium hydroxide to the phenolphthalein end point results only in neutralization of the free acid. This permits calculation of the free acid content of the solution. The difference between the two titration values is thus equivalent to the aluminum.

Scott's procedure should be modified by carrying the titration for free acid nearly to the point of precipitation of aluminum hydroxide before addition of fluoride.

Synder (42) proposed the determination of aluminum by neutralization of an acidified aluminum tartrate solution with barium hydroxide to the phenolphthalein end point. The solution is then treated with neutral potassium fluoride solution to precipitate potassium cryolite.

The caustic liberated by the conversion of the basic aluminum tartrate to cryolite is then titrated with standard acid. Synder stated that sodium hydroxide could not be used for the initial neutralization if satisfactory results are to be obtained.

Hale (43) reported that lithium hydroxide may be employed instead of barium hydroxide to effect the neutralization. He obtained poor results when using sodium hydroxide alone, but acceptable results were obtained if barium chloride was first added. The presence of barium was found to affect the nature of the soluble aluminum tartrate complex. The procedure is empirical and the aluminum factor for the standard acid must be found by standardization against a solution of known aluminum content. One cause of this is coprecipitation of some

liberated sodium hydroxide with cryolite.

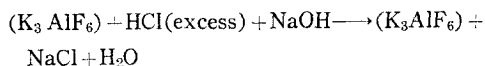
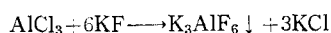
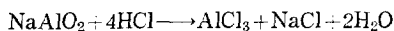
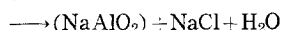
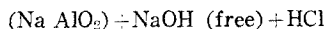
Thus, if potassium fluoride is added to a caustic aluminate solution—either in the presence or absence of tartrate—the subsequent total titration to phenolphthalein will be considerably less than theoretical. This is comparable to the occlusion of acid by cryolite that has been precipitated in acid solution.

The direct determination of aluminum by sodium hydroxide titration has been proposed by the Dow Chemical Co. (44) and the ASTM (45).

A method for determining aluminum was described by Bushey, A. H. (3) in which a caustic solution of aluminate is titrated with hydrochloric acid from pH of approximately 11 to 3.

The point at which the free caustic is neutralized and the reaction with aluminate starts (about pH 11) is identified by potentiometric measurements. The end point at which the conversion of the aluminum to the chloride is completed is identified visually and indirectly by an application of Scott's method with potassium fluoride.

The reactions involved are:



The average deviation from truth was 0.31%. A tenfold variation (0.02g~0.2g) in the quantity of aluminum titrated had no influence on the accuracy.

Similar volumetric methods for determining aluminum were discussed by Watts, H. L. (46) and Wilson et al (47). Sodium gluconate has been shown to be an effective complexing agent in volumetric analysis (48). This method has been applied to steels, high temperature alloys, and nonferrous alloys (49). Aluminum is separated from its alloy constituents by the mercury cathode prior to the titration. This



method is subject to possible errors in the presence of relatively large amounts zirconium and titanium.

A proposed ASTM method (50) for aluminum in high alloy steels removes interfering elements with a mercury cathode separation followed by an extraction of the cupferrates and a sodium hydroxide separation. Aluminum was precipitated with 8-hydroxyquinoline and subsequently titrated (51).

Přibil et al (52) discussed the chelometric estimation of aluminum and iron using CDTA [(1,2-cyclohexylene dinitrilo) tetraacetic acid].

Burke, K. E. et al (15) proposed to determine milligram quantities of aluminum in a wide variety of steels and experimental alloys by a titrimetric method using CDTA. The chelating ligand is not selective and hence separations are required before such a chelon can be applied to the estimation of aluminium in the presence of the many elements often found in morden alloys. A procedure was developed where in the mercury cathode is employed to remove most of the interfering elements; sodium chlorate was used for the conversion of manganese to manganese dioxide which was removed by filtration, along with the elements that were dehydrated with perchloric acid. For alloys containing titanium and zirconium, a tri-N-octylphosphine oxide, TOPO, liquid-liquid extraction was performed. The determination was completed with a backtitration of an excess of CDTA with a standard zinc solution to the Xylenol orange end point.

The mean absolute error was less than 0.02% for a multicomponent, high temperature alloy containing about 3% aluminum. Eight samples could be analysed for aluminum in a 7 hour day.

Přibil (53) has described a method for the simultaneous determination of aluminum and iron.

An excess of standard EDTA is added to the solution containing the two ions, the pH adjusted

to 5, and the excess EDTA titrated with standard iron (III) chloride solution. This gives total aluminum and iron. An excess of standard iron (III) chloride is then added to the solution, the pH adjusted to 2, and the excess iron determined iodometrically. Kritz (54) used pyrocatechol violet indicator in an EDTA determination of total aluminum and iron in glass.

Přibil and co-workers (54) have used EDTA in a potentiometric method for the determination of aluminum. Aluminum forms a stable complex with EDTA, particularly in solutions buffered at pH 5-6 with ammonium acetate. This fact makes possible an indirect potentiometric determination of the metal by a method based on the back titration of an excess of standard EDTA with a standard solution of iron (III) chloride. Aluminum can be determined by back titration of a measured excess of EDTA at pH 5.5, using as titrant a 0.1M zinc chloride solution containing a little copper (II) chloride. The end point is indicated by a violet color with Variamine Blue B in the presence of ammonium thiocyanate (55).

Kinnunen et al (56) have studied the use of disodium EDTA as a reagent for the titrimetric determination of aluminum in bronze and brass.

They report that the aluminum complex is readily formed by boiling an acidic aluminum solution with an excess of EDTA. Since the complex readily dissociates in ammoniacal solution at room temperature, it was found that for an indirect titration of aluminum, the excess EDTA must be titrated rapidly in a cool solution.

They further report that the end point of the titration of the excess EDTA is improved if a solution of manganese(II) sulfate is used as titrant with Eriochrom Black T as indicator (57).

As an alternative procedure, they report that

a zinc chloride solution may be used as the titrant with Zincon as indicator if the solution to be titrated is ice cold and ammoniacal (58).

Flaschka et al (59) have described a method for the microtitration of aluminum with EDTA.

The solution to be analyzed is treated with an excess of disodium EDTA, buffered to pH of about 4 with acetic acid and sodium acetate, and then the solution is back titrated at the boiling point with a standard thorium nitrate solution in the presence of Alizarin S indicator.

By this method 90–945  $\mu\text{g}$  of aluminum can be determined satisfactorily.

Amin (60) has used disodium EDTA for the determination of copper and aluminum in alloys.

The procedures are based on the use of thioacetamide as a precipitant for copper from a tartrate solution.

Milner et al (61) have used EDTA for the titrimetric determination of aluminum in non-ferrous alloys. Aluminum is first precipitated as aluminum benzoate. The precipitate is dissolved in hydrochloric acid, and titrated with 0.1M EDTA solution which has been standardized against an iron (III)chloride solution, using salicylic as indicator.

They have described a method for the determination of alumina (62) in rocks and refractories. This method depends upon precipitating aluminum with ammonium benzoate, dissolving the precipitate in hydrochloric acid, and titrating aluminum by the EDTA method previously described.

Amin et al (63) have described an EDTA method for the analysis of zinc-lead ores with thioacetamide and ion exchange resins. Aluminum may be titrated directly with disodium EDTA using Azurol S as indicator in a hot solution of pH 4. The end point may be determined either directly or by back titration of a small excess of the EDTA with an aluminum solution after addition of sodium acetate buffer.

Good results were obtained in experiments using 5.8–5.9 $\mu\text{g}$  of aluminum. This determination may be carried out in the presence of iron(III), calcium, magnesium, potassium, ammonium, manganese, and titanyl ions (64).

Taylor (65) has used hematoxylin as an indicator in the titration of aluminum with EDTA. In this way the necessity of a back titration of EDTA with other standard solutions is eliminated.

Hill (66) has described a method in which the properties of Eriochrome Cyanine R are so controlled that the reagent is made specific for aluminum by the combined use of sodium mercaptoacetate, EDTA, 8-hydroxyquinoline, or a fluoride.

## VII. Atomic absorption methods

The atomic absorption method for the determination of aluminum was developed to fill the need for a more rapid and accurate method than those described above. But many of the literatures reveal that atomic absorption spectroscopy has not been successful when applied to the determination of aluminum (67–72). One of the reasons for this failure appears to be the formation of the refractory AlO molecule in the flame thus leaving virtually no free atoms for atomic absorption.

Dowling, F.B. et al (73) reported that they succeeded in determining aluminum by atomic absorption spectroscopy using either oxy-acetylene or oxy-hydrogen flames fed with an organic aerosol containing an aluminum with both the flames by them (74).

They found that the oxy-acetylene flame is to be more sensitive than the oxy-hydrogen flame. That paper presented the results of the investigation of the parameters which govern the intensity of aluminum absorption when an oxy-acetylene flame is used. It has been reported that atomic absorption spectrophoto-

metry is not entirely free from chemical and spectral interferences (75-79), and these interferences are more likely when highly concentrated solutions of a given matrix are analyzed for a trace constituent.

For the atomic absorption method of determining aluminum in vanadium metal, Hansen, R. K. et al (10) used the commercially available equipment with the premixed nitrous oxide-acetylene flame burner for determinations over the range of 100 ppm to 1% aluminum. The important parameters which influenced the interference were flame stoichiometry, acid concentration, and aluminum concentration. This method has been successfully applied to the determination of aluminum (80-84) and Ramakrishna et al (80) reported observing no interference for the determination of 20  $\mu\text{g}$  aluminum/ml in the presence of 103  $\mu\text{g}$  vanadium/ml.

Dagnall, R.M. et al (86) described for the first time the atomic fluorescence characteristics of aluminum, using a commercially available flame spectrometer in conjunction with electronically modulated electrodeless discharge tube sources (89) and a nitrogen or argon separated nitrous oxide-acetylene flame. The determination of aluminum and vanadium by atomic fluorescence spectrometry is relatively free from interference effects and in a separated nitrous oxide-acetylene flame gives detection limits about one order of magnitude better than those obtained by conventional atomic absorption spectrometry using the same spectrometer.

### VIII. Activation Analysis

Activation analysis is generally considered to have its genesis in the classic papers of Hevesy and Levi in 1936 and of Seaborg and Livingood in 1938.

Determination of aluminum in a "nimonic" alloy by activation with fast neutrons was reported by Quigley, D. A. et al (13). It has shown that aluminum at the 6% level in a complex

matrix such as a nimonic alloy can be determined non-destructively by activation with fast neutrons with a precision comparable to that obtainable by atomic absorption spectroscopy (5-10%). The composition of the alloy investigated is shown in table III.

Table III - Composition of nimonic alloy

Element	Specification %	Chemical Analysis %
C	0.08-0.15	0.06
Mn	0.25max	0.02
Si	0.50max	0.01
Cr	12.5-14.5	13.5
Ni	balance	72.5
Co	1.0max	0.11
Mo	3.8-5.2	4.55
Nb+Ta	1.8-2.8	2.10
Ti	0.5-1.5	0.92
Al	5.5-6.5	6.34
Fe	2.0max	0.075
B	0.005-0.015	0.013
Zr	0.05-0.15	0.10
S	trace	0.013
P	trace	0.002

The determination of aluminum in titania powder and titanium metal can easily be done nondestructively by Neirinckx, R. et al (11), as the  $\gamma$ -ray energy of  $^{28}\text{Al}$  is 1,7789 MeV. The most energetic  $^{51}\text{Ti}$   $\gamma$ -ray is 0.9285 MeV, while, after 2 min. of reactor irradiation, the other impurities in titanium or titania rarely give rise to important activities in the high-energy region. The sensitivity can, however, be enhanced by the preseparation procedures, which make it possible to use larger samples (up to 1g), while the nondestructive procedure is restricted to about 50mg, because of the high  $^{51}\text{Ti}$  activity. For non-destructive determination limit of aluminum is 5  $\mu\text{g}$ . For the preseparation procedures the sensitivity is determined by the blank, namely 1  $\mu\text{g}$  for both the ion-exchange procedure and the

titanium hydroxide precipitation method.

Richardson, A. E. et al (14) used a mixture of 14.5-MeV and slow neutrons for the simultaneous determination of aluminum in solid composite propellants by nondestructive activation analysis with a precision of better than  $\pm 1\%$ . The method was developed and evaluated by carrying out a series of determinations on samples of known composition and comparing the results with those obtained by X-ray fluorescence.

Activation analysis has relatively minor matrix effects compared to those of X-ray fluorescence and can be more easily extended beyond the quality control limits to cover wide percentage ranges of the elements to which it is sensitive.

### K. Conclusion

Chemical analysis of aluminum has been rapidly developed since last few decades according to their economical and industrial importance of their elements.

The analytical methods of aluminum in various matrices have been used as a routine work in industrial laboratory in spite of the the often erratic results which were probably due to (a) incomplete separation of interfering ions, (b) interference of unknown ions, (c) aluminum contamination in different reagents, and (d) lengthy chemical procedures.

Conventional method such as a gravimetric, volumetric, spectrophotometric, fluorometric and spectrographic methods are quite useful for the major constituents of aluminum in the sample, but these method seem to be very dangerous to apply for the determination of submicro amount of aluminum as an impurity in high purity materials.

The neutron activation method is most promising method for those routine application for micro amount of aluminum determination. This method is very time saving and great accuracy

can be possibly expected by means of their high selectivity of particular nuclear reactions.

The price of the equipment is also agreeable compared with those conventional spectrographic method.

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