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Original Scientific Paper

Determination of Silver in Aluminum by Thin Layer Chromatography

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Small quantities of silver in technical aluminum can be determined by TLC on the layer of microcrystalline cellulose after separation and concentration by coprecipitation with CdS. The chromatograms were developed by a solvent composed of butanol-methanol-water-nitric acid in the proportion 80 : 5 : 10 : 5 (v/v). Visualisation was made with hydrogen sulfide. After scanning the obtained spots, concentration of silver in the samples was calculated by comparison with reference spots.

The presence of silver in aluminum is always artificial, and the silver content of an aluminum sample will depend on the latter's intended use. If silver is added to modify the general properties of aluminum, the silver content is fairly large and may be determined by any existing analytical method. If, however, the addition of silver is made to tag the aluminum so as to enable a follow up of the bulk of aluminum through a technological process, the silver content is small and its determination may be difficult. This particular case has been chosen to investigate the applicability of the thin-layer chromatographic approach for solving analogous problems.

EXPERIMENTAL

A sample of the technical aluminum material marked with silver (1 g) was dissolved in 40 ml of a mixture containing sulfuric and nitric acid diluted with water (30 : 10 : 60 v/v). After dissolving the sample 60 ml of water and 20 mg of Cd-acetate was added to the solution. The solution was then saturated with gaseous hydrogen sulfide. The precipitated cadmium sulfide containing coprecipitated silver and other heavy metals present in metal as impurities was collected on a filter and then dissolved in dilute nitric acid (1 : 2). This solution was reduced to a small volume by evaporation, and the residue was quantitatively transferred to a chromatographic plate².

Chromatography

Commercial 20 × 20 cm plates coated 0.1 mm thick with microcrystalline cellulose (product by E. Merck, Darmstadt, BRD) were used. Six spots, four references and two samples, were applied per plate, onto a starting line drawn 2 cm above the bottom. To separate the silver from other heavy metals coprecipitated with cadmium sulfide, chromatograms were developed in the usual way³ using a solvent system composed of n-butanol-methanol-water-nitric acid (80 : 5 : 10 : 5 v/v). Developed plates were dried in hot air, after which the spots were made visible by exposure to hydrogen sulfide gas (Figure 1a, 1b, 1c). The optimal

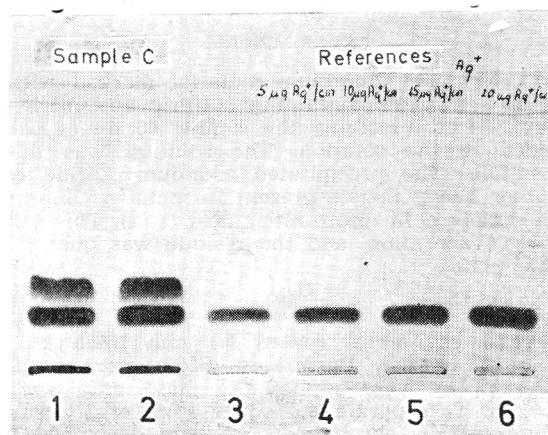
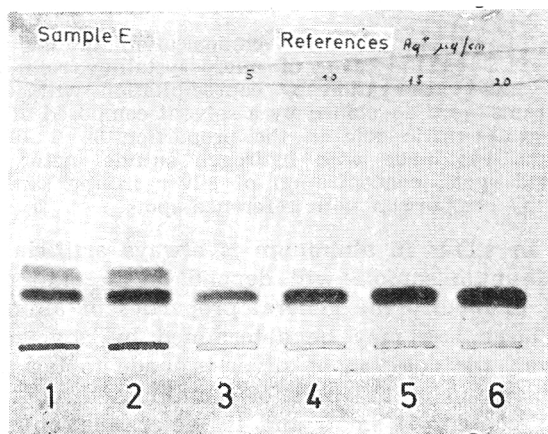
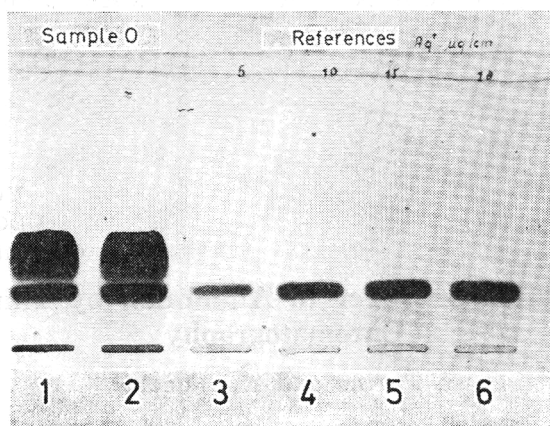


Figure 1. Thin layer chromatograms of the silver separated from samples of technical aluminum. The samples «O», «E», «C» are taken from technical aluminum marked with silver. Other heavy metal, copper, is present as an impurity and gives the spots over the silver.
 1, 2 — samples, 3, 4, 5 and 6 — references (5, 10, 15 and 20 $\mu\text{g Ag}$)

components ratio in the solvent were obtained by »symplex« mathematic method according to Deming⁴. The criterion was a resolution (Rs) between the silver and copper spots.

RESULTS

The spots were scanned with a CAMAG-TURNER scanning fluorimeter, and the area under the recorded curves was determined by the Monte Carlo method⁵. Data obtained by five parallel determinations are presented in the table (column 2) and corresponding amounts of silver in reference spots in column 1.

Results as the information on confidence limits of silver in the spots 1 and 2 were calculated by special treatment of data according to Snedecor⁶. (Figure 2).

TABLE

Plate A

			Y (rel. area)	\hat{Y} (regression)
1. Sample »O«	X ₀₁	μg Ag	132	—
2. Sample »O«	X ₀₂	μg Ag	128	—
3. Reference I	5	μg Ag	45	43.6
4. Reference II	10	μg Ag	88	92.1
5. Reference III	15	μg Ag	124	120.5
6. Reference IV	20	μg Ag	140	140.7

Regression curve: $\hat{Y} = 69.0 + 70 (\ln X)$

Standard deviation of reg. curve (for $\bar{Y} = 130$): $S_Y = 2.7$

Plate B

1. Sample »E«	X _{E1}	μg Ag	89	—
2. Sample »E«	X _{E2}	μg Ag	94	—
3. Reference I	5	μg Ag	50	49.5
4. Reference II	10	μg Ag	91	92.7
5. Reference III	15	μg Ag	120	117.9
6. Reference IV	20	μg Ag	135	135.8

Regression curve: $\hat{Y} = -50.5 + 62 (\ln X)$

Standard deviation of reg. curve (for $\bar{Y} = 91.5$): $S_Y = 0.9$

Plate C

1. Sample »C«	X _{C1}	μg Ag	111	—
2. Sample »C«	X _{C2}	μg Ag	117	—
3. Reference I	5	μg Ag	67	65.7
4. Reference II	10	μg Ag	95	96.7
5. Reference III	15	μg Ag	113	114.3
6. Reference IV	20	μg Ag	130	127.6

Regression curve: $\hat{Y} = -6.1 + 44.7 (\ln X)$

Standard deviation of reg. curve (for $\bar{Y} = 114$): $S_Y = 2.0$

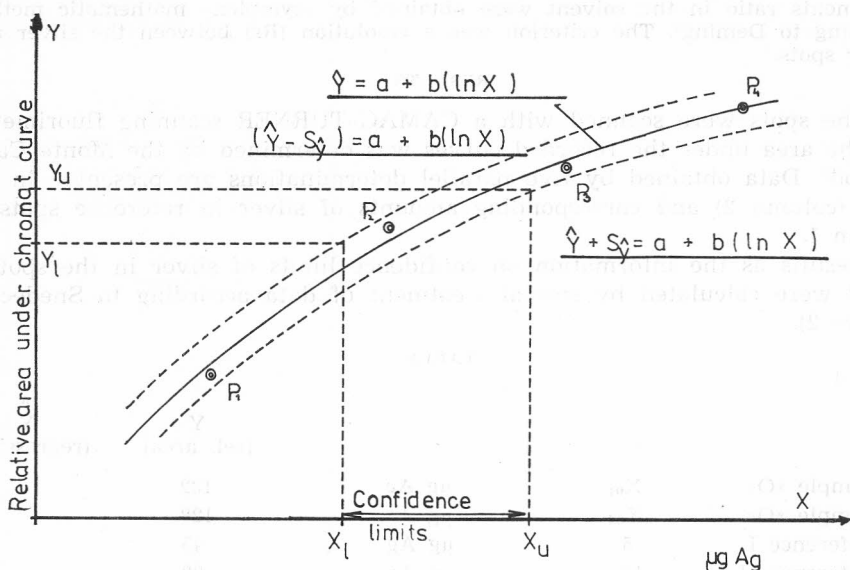


Figure 2. The relationship between amounts of Ag in the reference spots and relative area under chromatographic curves (full line). Dotted lines give the confidence limits of regression the curve. Points (P) are the plotted values of references.

Values of silver in samples »O«, »E« and »C« were calculated:

Sample »O«	$X_L = 15 \mu\text{g}; X_U = 20 \mu\text{g}$ (Ag in spots) Ag ... $0.0025 < X < 0.0020\%$ (in sample)
Sample »E«	$X_L = 8 \mu\text{g}; X = 12 \mu\text{g}$ (in spots) Ag ... $0.0008 < X < 0.0012\%$ (in sample)
Sample »C«	$X_L = 13 \mu\text{g}; X_U = 17 \mu\text{g}$ Ag (in spots) Ag ... $0.0013 < X < 0.0017\%$ (in sample)

DISCUSSION

The determination of small quantities of silver in aluminum was carried out satisfactory by the described method, although some other analytical methods can be applied as well. However, this approach coupling the coprecipitation and thin-layer chromatography, can be pursued in solving all similar problems. For successful coupling the chosen collector should not disturb the chromatographic process. The Cd-ions used in our case as the collector have a higher R_f value than concentrated heavy metals on chromatograms developed with the given solvent. The concentrated heavy metals can also be separated from the collector by using selective solvents or by combustion if cellulose or its derivatives serve as the collector.

REFERENCES

1. Š. Cerjan, S. Turina, *Analysis*, **2** (1973) 204.
2. N. Turina, S. Turina, *Chromatographia*, **11** (1978) 331.
3. E. Stahl, *Dünnschicht-Chromatographie*, Springer-Verlag, Berlin, 1962, p. 62.

4. S. N. Deming, S. L. Morgan, *Anal. Chem.* **45** (1973) 278A.
5. S. Turina, L. Klasinc, *Cromatographia*, **7** (1974) 203.
6. G. W. Snedecor, *Statistical methods*, Iowa State College Press, Ames Iowa, 1956, p. 122.

SAŽETAK

Određivanje srebra u aluminiju tankoslojnom kromatografijom

Srećko Turina i Nina Blažević

Za određivanje malih količina srebra u tehničkom aluminiju primijenjena je kvantitativna tankoslojna kromatografija. Srebro je najprije s ostalim teškim metalima izdvojeno od matičnog aluminija koprecipitacijom s kadmijevim sulfidom. Za kromatografsko razdvajanje korištena je kao podloga mikrokristalinična celuloza, a razvijач je bio sastavljen od butanola, metanola, vode i dušične kiseline u volumnom omjeru 80 : 5 : 10 : 5. Vizualizacija je izvršena pomoću sumporovodika. Mrlje su potom fotometriране, a koncentracija srebra u uzorcima tehničkog aluminija izračunata je na temelju uspoređivanja mrlja s referentnim mrljama.