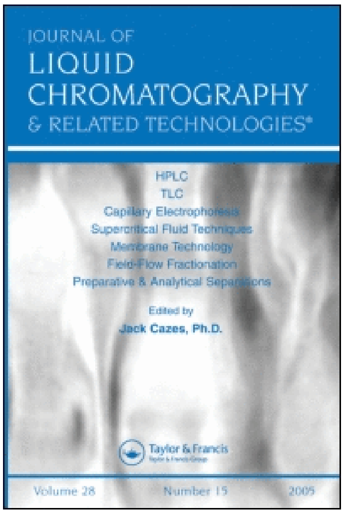

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Quantitative Determination of Mg in Ai-Alloys by Ion-Exchange TLC

M. Petrović[a]; M. Kaštelan-Macan[a]; S. Turina[b]; V. Ivanković[b]
[a] Laboratory for Analytical Chemistry Faculty of Chemical Engineering and Technology, University of Zagreb, Zagreb, Croatia [b] Faculty of Mechanical Engineering and Naval Architecture, University of Zagreb, Zagreb, Croatia

To cite this Article Petrović, M. , Kaštelan-Macan, M. , Turina, S. and Ivanković, V.(1993) 'Quantitative Determination of Mg in Ai-Alloys by Ion-Exchange TLC', Journal of Liquid Chromatography & Related Technologies, 16: 12, 2673 — 2684
To link to this Article: DOI: 10.1080/10826079308019602
URL: http://dx.doi.org/10.1080/10826079308019602

JOURNAL OF LIQUID CHROMATOGRAPHY, 16(12), 2673-2684 (1993)

QUANTITATIVE DETERMINATION OF Mg IN Al-ALLOYS BY ION-EXCHANGE TLC

M. PETROVIĆ[1], M. KAŠTELAN-MACAN[1], S. TURINA[2],
AND V. IVANKOVIĆ[2]
[1]*Laboratory for Analytical Chemistry*
Faculty of Chemical Engineering and Technology
University of Zagreb
Marulićev trg 20, 41000 Zagreb, Croatia
[2]*Faculty of Mechanical Engineering and Naval Architecture*
University of Zagreb
Marulićev trg 20, 41000 Zagreb, Croatia

ABSTRACT

Analytical procedure for the quantitative determination of Mg in Al-alloys using ion-exchange thin layer chromatography is described. Chromatographic plates were coated with Amberlite IRP-69 (strong-acid cation exchanger in H^+-form) mixed in different ratios with microcristalline cellulose. Solutions of HCl and HNO_3 respectively, in the concentration range from 0.5 - 2.0 mol dm^{-3} were used as developers. Chromatograms were visualized by spraying with ethanolic solution of 8-hydroxyquinoline and spots were scanned using Camag Turner Fluorometer 111. The optimal separation was obtained on TLC plates containing 23 % of ion-exchanger (particle size < 60 μm) and by eluting with 1.25 M HCl. R_F (Al)=0.12, R_F(Mg)=0.41.

INTRODUCTION

Due to their outstanding properties the light aluminium alloys have a remarkably wide field of application. They generally contain less than 15 % of added elements (Mg, Cu, Zn, Si, Mn) and standard methods for their determination comprise AAS, spectrography and spectrophotometry. Among other analytical techniques available, chromatographic methods offer some distinct advantages. In spite of the development of highly sophisticated techniques and expensive analytical equipment, thin layer chromatography is currently enjoying wide popularity as a simple, effective and low cost separation method for organic and inorganic substances. Since on standard cellulose layers a poor resolution of Mg and Al could be achieved, application of ion-exchangers as chromatographic layers gives good opportunity for their successful separation and quantitative "*in situ*" determination. Over the years, a variety of insoluble inorganic exchangers (phosphates, molybdates, tungstates and arsenates of Zr, Ti, Ce of Sn, amonium salts of heteropoly acids and hydrous oxides), synthetic liquid and solid cation and anion exchangers have been investigated as ion-exchange material in TLC [1]. The main advantage of ion-exchange TLC over conventional partion chromatography is the possibility of choosing an exchanger with high and specific selectivity for a given compound.

The aim of this study was to determine optimal conditions for the separation of magnesium and aluminium on cellulose layers modified by addition of solid cation exchanger Amberlite IRP-69. This method has been successfully utilized for the quantitative determination of magnesium in aluminium-based alloy where the amount of Mg varied form 0.5 - 5.0 %.

MATERIALS AND METHODS

A mixture of microcrystalline cellulose ("Merck") and different portions (5-23 %) of Amberlite IRP-69 was suspended in water, homogenized either by shaking or with an electric stirrer and spread on glass plates by Camag applicator. Amberlite IRP-69 ("Rohm and Haas"), a strongly acidic cation exchanger, was previously converted to H^+-form, sieved and fraction smaller than 60 μm was used. The tickness of wet layers was 0.3 mm. Experiments were performed on layers dried at room temperature.

Standard solutions containing 10-60 μg/mL of Al(III) and Mg(II) were prepared by dissolving $FeCl_3$ $6H_2O$ and $MgCl_2$ $6H_2O$, respectively in water.

10 μL of the solution of each cation and mixture of cations were spotted on plate and developed by ascending technique without previous saturation to a distance of 10 cm. The time of development differed according to the solvent system. Solutions of HCl and HNO_3, respectively, in the concentration range from 0.5 - 2.0 mol dm^{-3} were used as developers.

After developing chromatograms were dried and sprayed with ethanolic solution of 8-hydroxyquinoline (w=1 %), exposed to NH_3 vapours and sprayed with ethanolic solution of triethanolamine (w=5 %). The spots were detected by exciting fluorescence at 366 nm under UV-lamp.

Quantitative determination

Alloy samples (100-400 mg) were dissolved in NaOH. After filtration residues were dissolved in HCl (1:1) and diluted with distilled water to the volume of 50 mL. 10 μL aliquotes, same as 10 μL of standard mixtures, were applied to the chromatographic plate as narrow bands (1.5 cm long). After visualization quantitative determination was carried out using Camag Turner Fluorometer 111 (Muttenz, Switzerland).

For the spectrographic determination of Mg a spectrometar "Spectrumat 750 GDS-Leco" was used.

RESULTS AND DISCUSSION

Preliminary experiments were carried out on plain cellulose layers. The results, presented in TABLE 1, show that descrete spots of Al(III) and Mg(II) are difficult to obtain. Although, in some cases (solvent systems containing butanol) a fair degree of separation was achieved, development time for these solvent systems was at least 3 hours.

R_S-value, as a measure for resolution of two spots, is determined by dividing the distance between the centers of two adjacent spots by mean

TABLE 1.

R_F-values of Al(III) and Mg(II) on cellulose layers

Solvent system	R_F		Rs	development time [min]
	Al(III)	Mg(II)		
1.butanol+HC+H_2O 20:5:5,v/v	0.20	0.28	1.25	220
2. butanol+methanol+HCl+H_2O 30:15:30:10, v/v	0.51	0.59	1.10	180
3. butanol+ethylacetate+HAc 50:20:5, v/v	0.14	0.21	1.00	190
4. ethanol+HCl+H_2O 60:1:5,v/v	0.43	0.39	0.57	90
5. methanol+HCl+H_2O 40:5:5,v/v	0.74	0.69	0.71	70
6. acetone+HCl+H_2O 40:20:15,v/v	0.51	0.55	0.67	80

band width of developed spots [2]. In order to separate a neighboring pair of substances R_S-value must be higher than 0.8, but for quantitative "*in situ*" determination $R_S > 1.3$ is required [3].

One of possibilities to obtaine improved resolution is application of solid cation-exchangers as support in thin layer chromatography. Because of significant difference between K_d-values (distribution coefficients of Al(III) and Mg(II) on sulphonated polystyrene resins in HCl and HNO_3 media)[4] successful separation of Mg and Al could be obtained. The great similarity between the process in conventional column ion-exchange techniques and TLC technique considered here has to be emphasized. In the case of planar ion-exchange chromatography, microcristalline cellulose is used only as a binder.

The layers of Amberlite IRP-69, prepared in our laboratory are suitable for direct fluorimetric determination. It is important to maintain identical conditions

TABLE 2.
R_F-values of Al(III) and Mg(II) using aqueous solution of HCl as developer

Solvent system	Metal ion	Mass fraction of Amberlite IRP-69 in the layer % 9.0	13.0	16.7	20.0	23.0
0.75 M HCl	Al	0.34 T	0.12 T	0.09	0.05	0
	Mg	0.55 T	0.50 T	0.33	0.21	0.11
1.00 M HCl	Al	0.47	0.19	0.17	0.12	0.05
	Mg	0.60	0.55 T	0.49	0.41	0.29
1.25 M HCl	Al	0.55	0.37	0.25	0.16	0.12
	Mg	0.75	0.64 T	0.55	0.44	0.41
1.50 M HCl	Al	0.60 T	0.50	0.36	0.28	0.22
	Mg	0.85	0.79 T	0.65	0.60	0.59
1.75 M HCl	Al	0.69 T	0.51 T	0.45 T	0.41	0.40
	Mg	0.92	0.81 T	0.74	0.68	0.65

T-tailed

of layer preparation. The most important factor that ensure uniform and compact layer is grain size of solid ion-exchanger. To prevent spot tailing, we crushed in powder commercially available Amberlite IRP-69 (100-500 mesh), sieved it and fraction with particle size smaller than 60 μm was used.

R_F-values obtained on thin layers with different mass fraction of Amberlite IRP-69 and aqueous solutions of HCl and HNO_3 as eluens, are listed in TABLES 2 and 3.

TABLE 3.

RF-values of Al(III) and Mg(II) using aqueous solution of HNO_3 as developer

Solvent system	Metal ion	Mass fraction of Amberlite IRP-69 in the layer % 9.0	13.0	16.7	20.0	23.0
0.75 M HNO_3	Al	0.14	0.09	0.07	0.05	0.02
	Mg	0.33	0.28	0.20	0.13	0.11
1.00 M HNO_3	Al	0.17	0.10	0.09	0.06	0.04
	Mg	0.36 T	0.32 T	0.25	0.16	0.13
1.25 M HNO_3	Al	0.35 T	0.28 T	0.21	0.13	0.12
	Mg	0.58	0.52 T	0.46	0.36	0.33
1.50 M HNO_3	Al	0.41 T	0.30	0.27	0.25	0.18
	Mg	0.67 T	0.61 T	0.55	0.54	0.43
1.75 M HNO_3	Al	0.49 T	0.41 T	0.37	0.35	0.21
	Mg	0.72 T	0.67 T	0.64	0.60	0.46

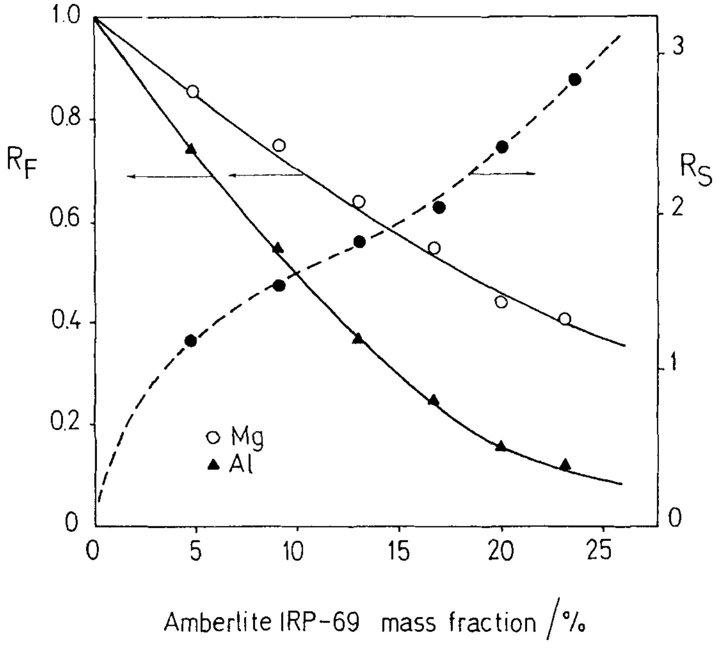

FIGURE 1. R_F and R_S-values as functions of mass fraction of Amberlite IRP-69 in the layer; solvent system: 1.25 M HCl

The best separation expressed as R_S-value > 2, was achieved on plates containing 23 % of cation exchanger and with c(HCl)=1.25 mol dm $^{-3}$ (Fig. 1 and 2). The spots were completely separated, compact, small and without tails. Development time was 30 minutes.

In further experiments influence of organic solvents (ethanol and acetone) was studied. The effect of organic solvents on resolution of Al and Mg spots on chromatographic plates containing 20 % of Amberlite IRP-69 is shown in Fig. 3. The results obtained indicate that, in contrast to aqueous solution of HNO_3, addition of ethanol and especially addition of acetone leads to reduction of R_S-values. The same results were obtained by testing HCl as eluens.

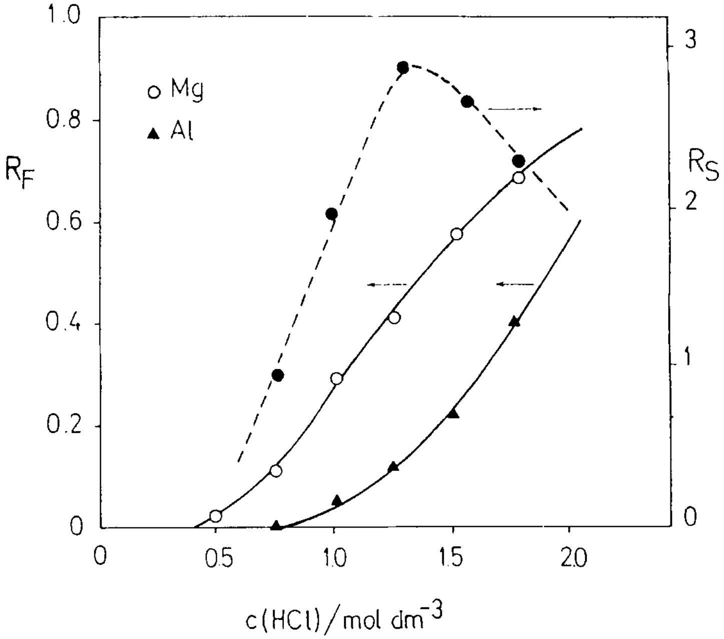

FIGURE 2. R_F and R_S-values as functions of HCl concentration in the solvent; layer: cellulose containing 23.0 % of Amberlite IRP-69

For the quantitative determination calibration graph of peak area against concentration of magnesium in standard mixtures was plotted. Each peak was recorded twice, and from the obtained chromatogram profiles, area under the chromatographic curves were determined by the Monte Carlo method [5]. It was found that the best regression curve for magnesium can be expressed by the function $y = 56.88\ x + 0.35$, with correlation coefficient $r=0.9942$.

Since amount of magnesium in Al-Mg alloys can vary from 0.2 - 10 % , the minimal quantity of Mg and the highest ratio of Al/Mg which can still be detected was determined. Standard mixtures with increasing concentrations

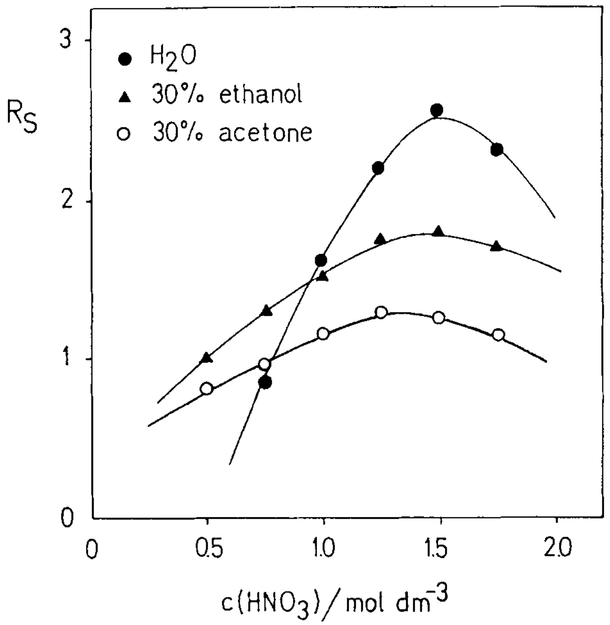

FIGURE 3. R_S-values as a function of HNO_3 concentration in various solvent systems; layer: cellulose containing 20.0 % of Amberlite IRP-69

of magnesium (5-500 µg/mL) were applied on plate containing 23 % of Amberlite IRP-69, while the concentration of aluminium (200 µg/mL) was constant. The minimal quantity of Mg which can still be determined with good confidence by measuring fluorescence is 10 µg/mL (0.1 µg/spot) and Al/Mg ratio 20:1. Fluorescence scans are shown in Fig. 4. In the case of alloys with higher Al/Mg ratio (20:1-200:1) preliminary removal of Al is required.

Concerning the presence of alloying elements, another ions (Cu, Fe, Mn, Zn and Ti) were found to have negligible interference in the determination of Mg in aluminium-base alloys.

The proposed method was tested on different AlMg alloys (TABLE 4.). The repeatability and accuracy were checked by applying on the same plate

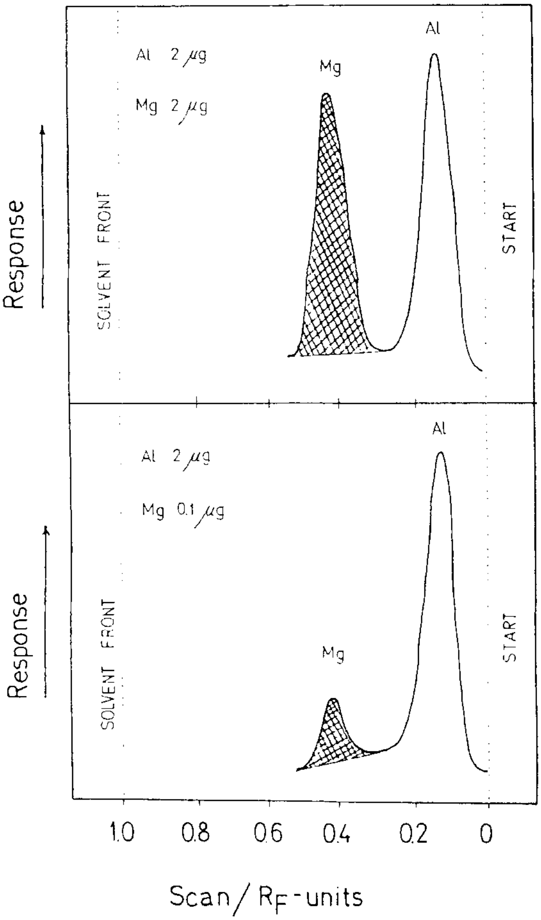

FIGURE 4. Fluorescence scans of Al(III) and Mg(II) mixtures
A) Al:Mg = 1:1
B) Al:Mg = 20:1
Layer: cellulose containing 23.0 % of Amberlite IRP-69
Solvent system: 1.25 M HCl

TABLE 4.
Comparation of quantitative determination of Mg in different AlMg-alloys by QTLC and spectrography

	Mg / %		
Alloy	Spectrography	QTLC	Error/ %
1. AlMg0.5	0.68	0.63	-7.49
2. AlMg1.05	1.20	1.14	-5.24
3. AlMg2.05	2.07	1.95	-5.80
4. AlMg2.72	2.28	2.39	+4.87
5. AlMg5	4.50	4.62	+2.58

three loadings of sample solutions. The results were compared with those obtained by spectrographic measurements. On the basis of the statistical evaluation of the data obtained this method has been shown to be accurate and reliable for the quantitative determination of magnesium in aluminium rich alloys. Futhermore, it can be easily applied in the laboratory practice as it is simple and no expensive instruments are required for its performance.

REFERENCES

1. G.Grassini-Strazza, J.Chromatogr. 466, 1 (1989)

2. F.Geiss, Fundamentals of Thin Layer Chromatography (Planar Chromatography), A.Huting Verlag, Heidelberg, 1987

3. S.Turina, Tankoslojna kromatografija, SKTH/Kem.Ind. Zagreb, 1984

4. F.W.Strelow. R.Rethemeyer, C.J.C.Bothma, Anal.Chem. 37, 106 (1965)

5. S.Turina. L.Klasinc, Chromatographia, 7, 203 (1974)

Received: December 9, 1992
Accepted: January 13, 1993