



Lecture Ga(III)

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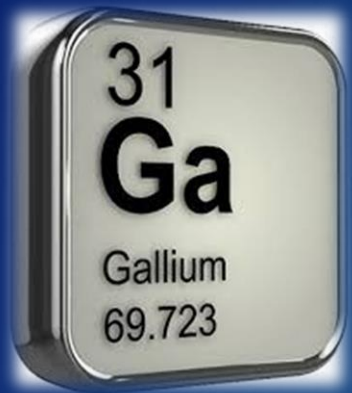
**“EXTRACTION-CHROMOGENIC SYSTEMS FOR GALLIUM(III) BASED ON AZO DYES
AND XYLOMETAZOLINE HYDROCHLORIDE,,**

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Gallium



Gallium — is a group 13 post-transition metal, position 31 in the periodic table.

Its physical and chemical properties were successfully predicted by Dmitri Mendeleev in 1871, several years before its actual discovery in a sample of sphalerite (1875).

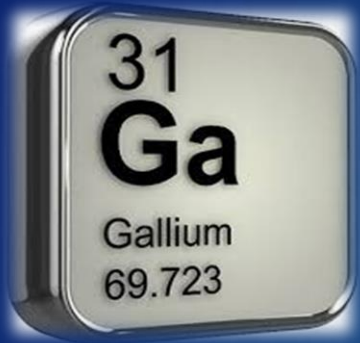
Until the semiconductor boom, gallium's main application was in the production of metal alloys and high-temperature thermometers.

Gallium nowadays – it is of strategic importance for various branches of technology and science and has been described in the literature as the "**backbone of the electronics industry**". Due to its unique properties, gallium can hardly be replaced by other materials for most of its applications, especially in **microelectronics**, **optics**, **solar energy conversion**, **data storage**, **neutrino detection experiments**, **low-freezing-point alloys** and **medicine**.



Gallium characterization

- **Gallium** — p-element, position 31, 13 group in the periodic table;
- **Gallium** — is a soft, brittle metal of silver-white (according to other sources, light gray) color with a bluish tint;
- ✓ As gallium solidifies, its volume increases. This property is very rare.
- ✓ Natural gallium consists of two stable isotopes ^{69}Ga (60,11 ат. %) и ^{71}Ga (39,89 ат. %).
- ✓ Advantage of **gallium** is the wide temperature range of existence of the liquid state (30°C – 2204°C).



Gallium occurrence



Gallium is a typical trace element with a dual geochemical nature, dispersed rare element in the Earth's crust.

Gallium – the 34th most abundant element on Earth.

Due to the similarity of its crystal chemical properties with the main rock-forming elements (Al, Fe, etc.) and the wide possibility of isomorphism with them, gallium does not form large accumulations.

It is present in trace amounts in most silicate rocks, however minerals, such as gallite (CuGaS_2) and söhngelite ($\text{Ga}(\text{OH})_3$), in which it is a major component, are quite rare; usually extracted as a by-product of the aluminum and zinc production. However, to ensure long-term supply of this element, enough to meet the growing future demands, new investments, additional sources, and appropriate recycling and analytical procedures are needed.

- **In the Earth's crust** – average content – 19 g t^{-1} ;
- **In the water of the oceans** – $3 \cdot 10^{-5} \text{ mg L}^{-1}$;





Gallium biology

Gallium – does not play a biological role.

Contact of the skin with gallium leads to the fact that ultra-small dispersed particles of the metal remain on it. Outwardly it looks like a gray spot. When you try to remove it, it smears even more. The best way to remove stains from your hands or surfaces – to use liquid soap.

Gallium is low-toxic according to some sources, highly toxic according to others.

Gallium in analytical techniques

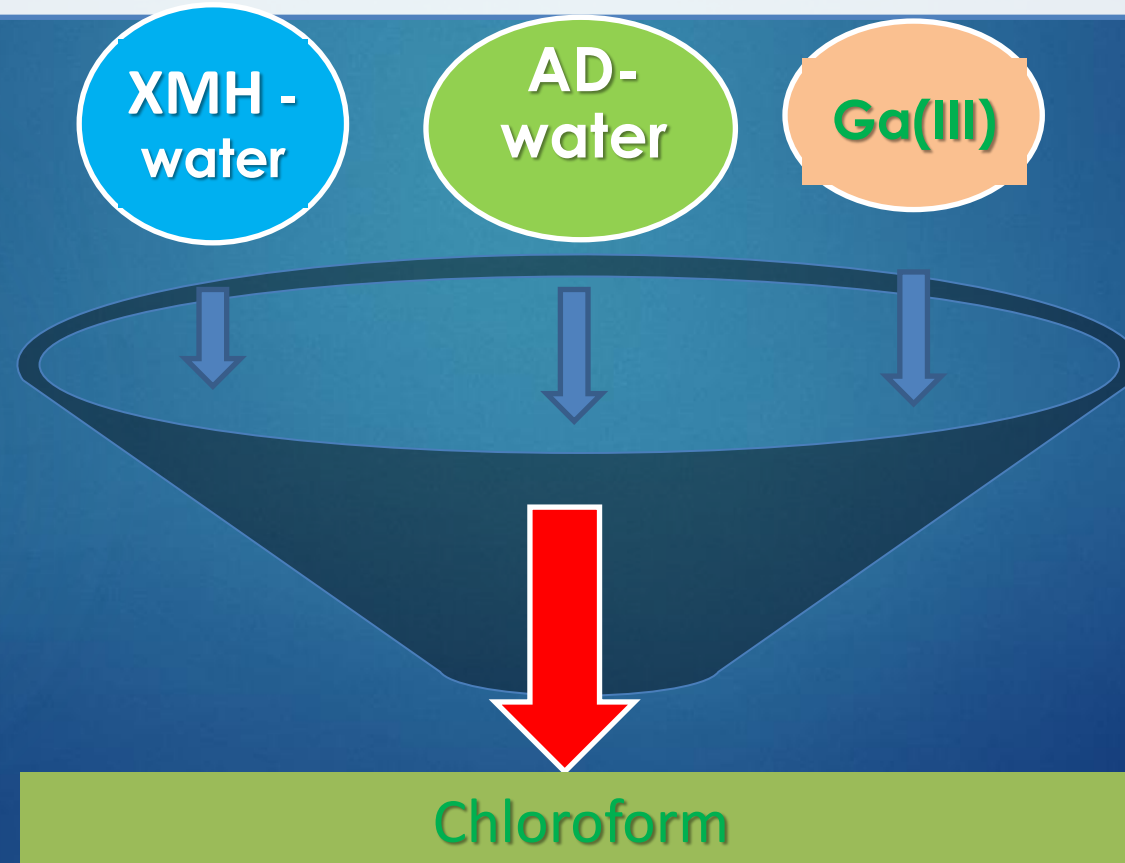
Methods involving spectrophotometry

- simple and low-cost;
- can be easily combined with procedures for preliminary separation and concentration;
- can be easily combined with cloud point extraction;
- can be easily combined with liquid-liquid extraction.



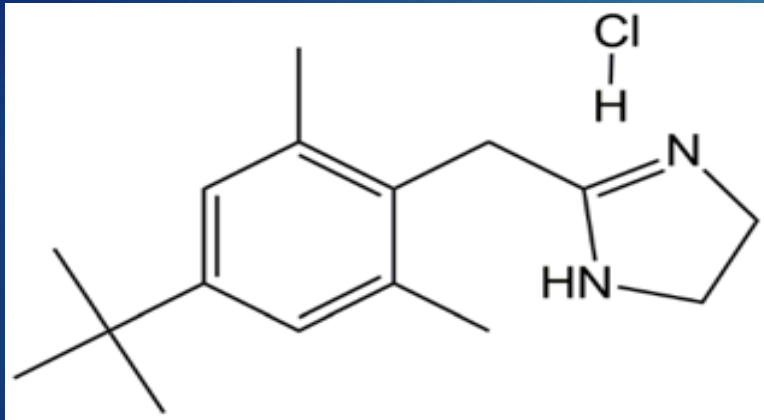
The aim of the present work is:

- describe investigations on liquid-liquid extraction systems involving GaIII, AD, XMH, water and chloroform. The ADs selected were 4-(2-pyridylazo)resorcinol (PAR) and 4-(2-thiazolylazo)resorcinol (TAR).



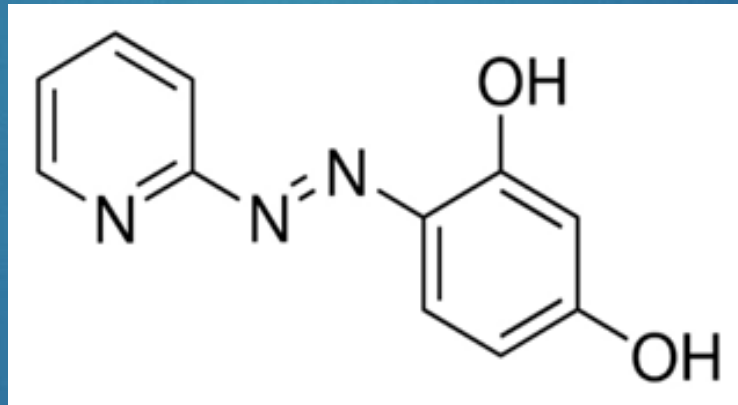
Reagents and apparatus

- **XMH** – a well-known analytical reagent;
- **4-(2-Pyridylazo)resorcinol (PAR)** – has been used in biological and analytical practice.
- **4-(2-Thiazolylazo)resorcinol (TAR)** – a well-known analytical reagent;



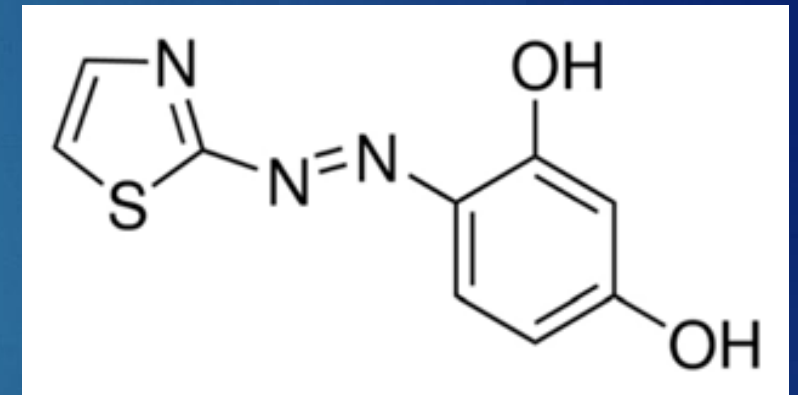
XMH

2-[4-(1,1-Dimethylethyl)-
2,6dimethylbenzyl]-4,5-dihydro-1*H*-
imidazole hydrochloride;
Xylometazoline hydrochloride



PAR

4-(2-Pyridylazo)resorcinol



TAR

4-(2-Thiazolylazo)resorcinol

Reagents and apparatus

- **Solution of Ga^{III}** ($c_{\text{Ga(III)}} = 1 \times 10^{-4} \text{ mol dm}^{-3}$) was prepared by dissolving Ga₂O₃ (Koch-Light Laboratories Ltd., 99,99 %) in a hot conc. HCl solution (20 cm³)..
- **ADs (PAR, 99 % and TAR, 97 %)** (p.a., Merck, Germany) – aqueous solutions with concentrations of $7.5 \times 10^{-3} \text{ mol dm}^{-3}$ were used.
- **XMH (purity $\geq 99 \%$)** (p.a., Merck, Germany) – aqueous solutions with concentrations of $2.4 \times 10^{-3} \text{ mol dm}^{-3}$ were used.
- The acidity of **the aqueous medium** was set by the addition of buffer solution, prepared by mixing 2.0 mol dm^{-3} aqueous solutions of CH₃COOH and ammonia.
- **WTW InoLab 720 pH-meter (Germany)** – pH was measured.
- **Absorbance** was measured using a **Ultrospec3300 pro UV-Vis spectrophotometers (UK)**, equipped with 10-mm path-length cells.
- Distilled water and redistilled chloroform were used in all experiments.

Results and Discussion

1. Liquid-liquid extraction-spectrophotometric optimization 1.1. Absorption spectra of complex in chloroform

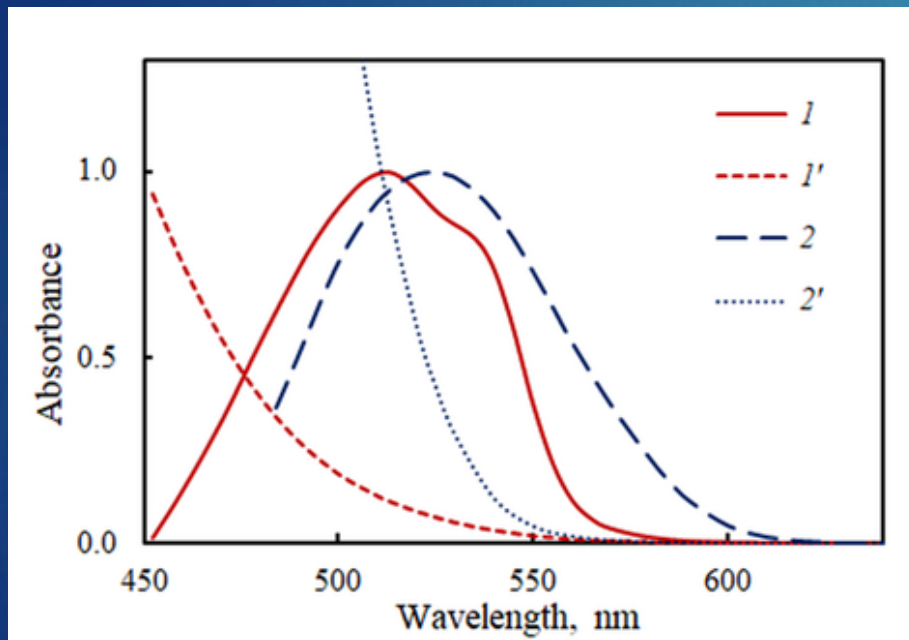


Figure 1. Absorption spectra in chloroform of the Ga^{III}-AD-XMH complexes against blanks (1, 2) [$c_{\text{Ga}} = 1 \times 10^{-5} \text{ mol dm}^{-3}$ (1) or $2 \times 10^{-5} \text{ mol dm}^{-3}$ (2)] and blanks (AD-XMH) against chloroform (1' and 2').

(1, 1') $c_{\text{PAR}} = 1.2 \times 10^{-4} \text{ mol dm}^{-3}$, $c_{\text{XMH}} = 2 \times 10^{-3} \text{ mol dm}^{-3}$, pH 5.7, $t_{\text{ex}} = 15 \text{ sec}$;
(2, 2') $c_{\text{TAR}} = 2.8 \times 10^{-4} \text{ mol dm}^{-3}$, $c_{\text{XMH}} = 2 \times 10^{-3} \text{ mol dm}^{-3}$, pH 5.4, $t_{\text{ex}} = 90 \text{ sec}$.

Under the optimum conditions (Table 1), the complex with PAR has an absorption maximum at 512 nm.

Under the optimum conditions (Table 1), the complex with TAR has an absorption maximum at 525 nm.

Results and Discussion

1.2. Effect of the pH

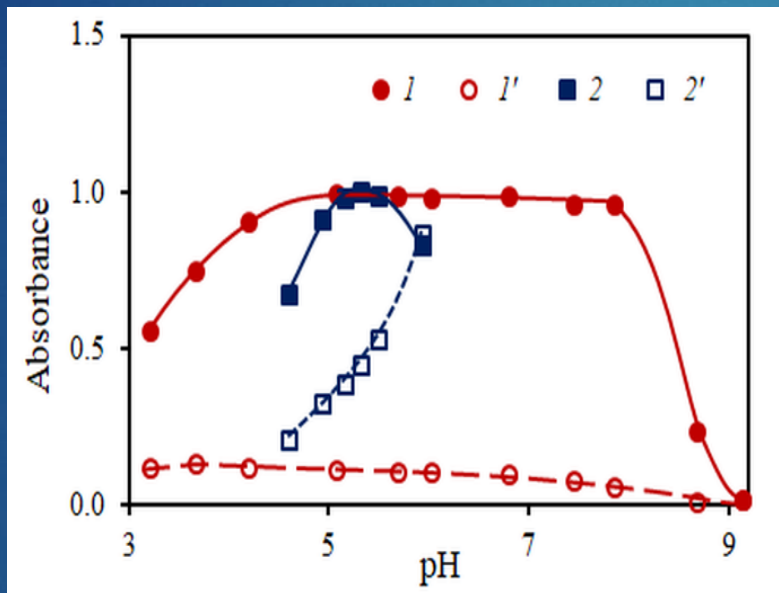


Figure 2. Absorbance of the Ga^{III}-AD-XMZ complexes vs pH of the aqueous phase.

(1) $c_{Ga} = 1 \times 10^{-5} \text{ mol dm}^{-3}$, $c_{PAR} = 1.2 \times 10^{-4} \text{ mol dm}^{-3}$, $c_{XMH} = 2 \times 10^{-3} \text{ mol dm}^{-3}$, $t_{ex} = 15 \text{ sec}$, $\lambda = 512 \text{ nm}$;

(2) $c_{Ga} = 2 \times 10^{-5} \text{ mol dm}^{-3}$, $c_{TAR} = 2.8 \times 10^{-4} \text{ mol dm}^{-3}$, $c_{XMH} = 2 \times 10^{-3} \text{ mol dm}^{-3}$, $t_{ex} = 90 \text{ sec}$, $\lambda = 525 \text{ nm}$.

Absorbance is maximal in the range of pH 5.5-6.

Results and Discussion

1.3. Effect of reagents concentration

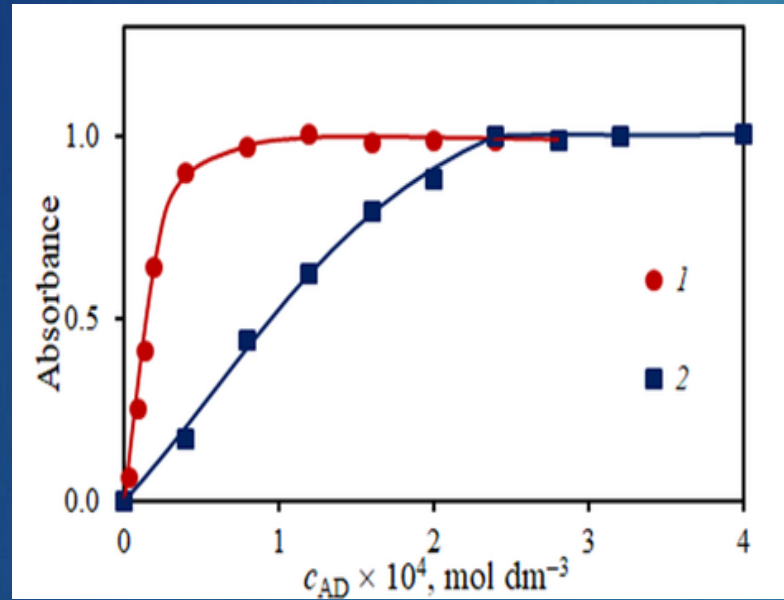


Figure 3. Effect of AD concentration.

1 - $c_{Ga} = 1 \times 10^{-5} \text{ mol dm}^{-3}$, $c_{XMH} = 2 \times 10^{-3} \text{ mol dm}^{-3}$, pH 5.7, $t_{ex} = 15 \text{ sec}$, $\lambda = 512 \text{ nm}$;

2 - $c_{Ga} = 2 \times 10^{-5} \text{ mol dm}^{-3}$, $c_{XMH} = 2 \times 10^{-3} \text{ mol dm}^{-3}$, pH 5.4, $t_{ex} = 90 \text{ sec}$, $\lambda = 525 \text{ nm}$.

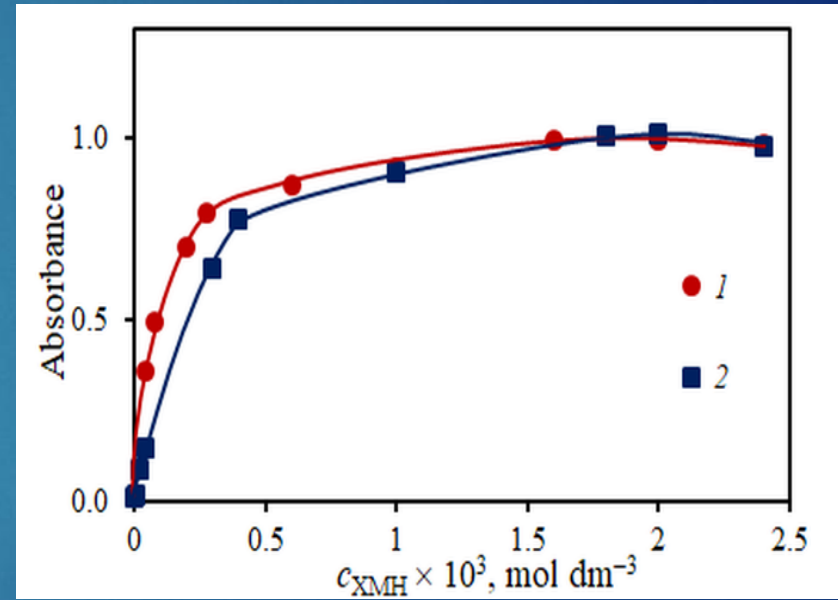


Figure 4. Effect of XMH concentration.

1 - $c_{Ga} = 1 \times 10^{-5} \text{ mol dm}^{-3}$, $c_{PAR} = 1.2 \times 10^{-4} \text{ mol dm}^{-3}$, pH 5.7, $t_{ex} = 15 \text{ sec}$, $\lambda = 512 \text{ nm}$;

2 - $c_{Ga} = 2 \times 10^{-5} \text{ mol dm}^{-3}$, $c_{TAR} = 2.8 \times 10^{-4} \text{ mol dm}^{-3}$, pH 5.4, $t_{ex} = 90 \text{ sec}$, $\lambda = 525 \text{ nm}$.

Ga(III) – AD – XMH

2. Optimum conditions for extraction

Extraction system	λ_{\max} , nm	pH	C_{AD} , mol dm ⁻³	C_{XMH} , mol dm ⁻³	Shaking time, sec	Extraction system
Ga ^{III} –PAR–XMH	512	5.7	1.2×10^{-4}	2.0×10^{-3}	15	Ga ^{III} –PAR–XMH
Ga ^{III} –TAR–XMH	525	5.4	2.8×10^{-4}	2.0×10^{-3}	90	Ga ^{III} –TAR–XMH

Table 1. Optimum operating conditions

Ga(III) – AD – XMH

3. Molar Ratios

3.1. Molar ratios, formulae and equations

Molar ratio	Mobile equilibrium method	Asmus' method	Bent-French method
PAR:Ga	2:1	2:1	Not applicable*
TAR:Ga	2:1	2:1	Not applicable*
XMH:Ga (AD = PAR)	1:1	1:1	Not applicable*

Table 2. Molar ratios in the ternary Ga^{III}-AD-XMH complexes obtained by different methods

The results show that the composition of the two complexes is Ga:AD:XMH = 1:2:1.
There are no indications that the complex formation is complicated by hydrolysis,

Results and Discussion

3.2. Extraction Characteristics

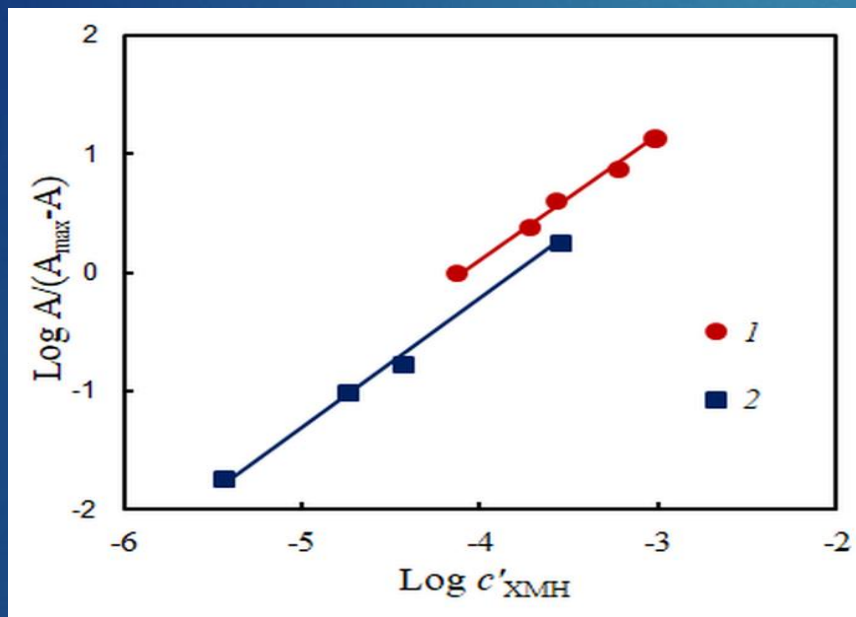


Figure 5. Straight lines obtained by the mobile equilibrium method:

(1) AD = PAR; $y = 0.99x + 4.09$, $R^2 = 0.9947$; (2) AD = TAR; $y = 1.04x + 3.91$, $R^2 = 0.9969$.

For the experimental conditions see Fig. 4.

Anionic chelates are formed by mixing solutions of Ga^{III} and AD and raising the pH to the optimum value. Their extraction into the organic phase in the presence of XMH can be represented by the following equation:



Ga(III) – AD – XMH

3.2. Extraction Characteristics

Extraction system	Log K_{ex}	Log D	$E\%$
Ga ^{III} –PAR–XMH	4.1 ± 0.1 ($N = 5$) ^a 4.10 ± 0.04 ($N = 5$) ^b	1.5 ± 0.3 ($N = 3$)	97 ± 1 ($N = 3$)
Ga ^{III} –TAR–XMH	3.8 ± 0.2 ($N = 4$) ^a 3.8 ± 0.1 ($N = 5$) ^b	1.5 ± 0.2 ($N = 4$)	97 ± 1 ($N = 4$)

^a Molar equilibrium method

^b Holme-Langmyhr method

Table 3. Obtained values of the extraction constants (K_{ex}), distribution ratios (D) and fractions extracted ($E\%$).

Ga(III) – AD – XMH

3.3. Analytical characteristics

Characteristics	Ga ^{III} –PAR–XMH	Ga ^{III} –TAR–XMH
Molar absorptivity (ϵ), dm ³ mol ⁻¹ cm ⁻¹	9.9×10^4	4.9×10^4
Sandell's sensitivity, ng cm ⁻²	0.68	1.46
Adherence to Beer's law, ng cm ⁻³	9.4 – 700	140 – 1670
Linear regression equation $y = ax + b$	$y = 1.416x + 0.009$ ($R = 0.9994$; $N = 6$)	$y = 0.707x - 0.009$ ($R = 0.9994$; $N = 6$)
Standard deviations of the slope (a) and y-intercept (b)	0.024; 0.009	0.012; 0.011
Limit of detection (LOD), ng cm ⁻³	2.8	42
Limit of quantitation (LOQ), ng cm ⁻³	9.4	140
Characteristics	Ga ^{III} –PAR–XMH	Ga ^{III} –TAR–XMH

Table 4. Analytical characteristics.

Gallium(III) – AD – XMH

5. Conclusions

- **Ga^{III}** forms well chloroform-extractable ternary complexes with the couples PAR-XMH and TAR-XMH.
- Complexes can be represented by the general formula $(XMZ^+)[Ga^{III}(AD)_2]$, where AD is the doubly deprotonated form (AD^{2-}) of PAR or TAR.
- Under the optimum conditions, the fractions extracted of these complexes are equal ($E=97\%$), but the $(XMZ^+)[Ga^{III}(PAR)_2]$ is more suitable for spectrophotometric purposes. It is more intensely colored, and the blank is low, repeatable and virtually unaffected by changes in pH. The shorter shaking time is another advantage of the system involving PAR.

Thank you for your attention