

# Determination of Aluminium, Chromium, Iron and Selenium Chelates in Drinking Water at Tikreet City by Gas Liquid Chromatography Technique with Electron Capture Detector



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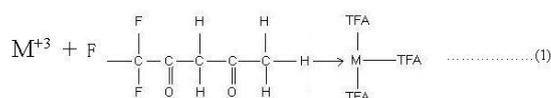
## ABSTRACT

Aluminum (III) ,and chromium (III) were chelated with trifluoroacetylacetonate (TFA), determined by gas liquid chromatography (GLC) with electron capture detector (ECD), while iron (III) was treated similarly ; but their chromatography suffered from number of practical difficulties . The technique was reliable for aluminum; although very sensitive was quite time consuming. Selenium was converted to the 4-chloropiazselenol and extracted into toluene for analysis. The Se (VI) was first reduced to Se (IV) by adding HCl and HBr with heating for more than 2 hours at 100 C°. Estimation of selenium by gas liquid chromatography with ECD considers very sensitive technique allowing pictogram (10<sup>-12</sup>gm) amount of selenium can be determined. The analysis of the sample (Drinking water at Tikreet city) was shown that the level of Al, Cr, Fe, Se in water below the detection limit of GLC with ECD.

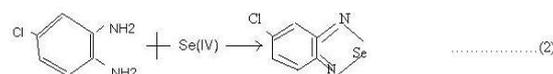
## Introduction

The application of gas chromatography to metal determination requires that the metal compounds which are usually ionic be converted to volatile compounds this can then be subjected to gas chromatographic separation and measurement [1].

The formation of volatile compounds {Equations(1) and (2)} are an important aspect of the analytical technique, it is necessary that the metal chelated be formed quantitatively , rapidly and also be easy to extract into organic solvents in order to facilitate injection in gas chromatography. The determination of metal chelated by gas chromatography is dependent upon the choice of support, stationary phase and the type of detector [2]. It is clear that all the fluorinated and chlorinated complexes form chelated with trivalent metals such as Al, Cr, Fe and tetravalent element (Se) which afford detection limits in the anagram range [2] .



M=Al , Fe and Cr  
TFA= 1,1,1 Tri fluoracetacetylacetonate



Di - amine chlorobenzene                      Selenium Chloropiazselenol

Estimation of Al,Cr,Fe and Se by gas liquid chromatography (GLC) with ECD are always based on the measurement of the amount of metal complexes formed by reaction of metal with an appropriate reagent in acid media , followed by extraction into toluene [3]. The introduction of second electrophone into the molecule such as chloride considerably improves the sensitivity allowing pictogram (10<sup>-12</sup> gm) amount of selenium to be determined [4] . Iron (III) and molybdenum (VI) interfere in the estimation of selenium with these reagent, but the interference can be overcome by addition of EDTA in both cases.

Vanadium (V) interferes with the metal chelated and unfortunately EDTA does not eliminate the interference [5].

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The level of selenium in blood was determined by using GLC with ECD [6] ; In present work , selenium in water was estimated by forming piaszelenol with chelating agent after reduction of Se (VI) to Se (IV) by heating with concentrated HCl and extraction into toluene [7] . Many workers [8] have been used gas chromatography of metals chelates for determination of aluminum, chromium and iron in different sample matrix; therefore these metals chelated have been used later in the present work for estimation of Al, Cr, Fe and Se in water.

## Results

All glassware was washed with water, detergent solution, rinsed with tap water and placed in a tank of 40% v/v aqueous nitric acid for at least 4 hours before use. The apparatus was then rinsed with distilled water , followed by double distilled water (DDW) and either dried by air drying or oven dried when required for immediate use . Syringes were immersed in acetone and ultrasonicated every day before injection was made.

The "Analar" grade reagent were used; nitric acid , hydrochloric acid , selenium dioxide , chromium nitrate , Aluminum nitrate , Ferric Chloride , Trifluoroacetate and 1,2 diamino-4-chlorobenzene .

## Synthesis of Metal Chelated

**Aluminum Trifluoroacetylacetate.:** Aluminum nitrate (25g) and sodium acetate (15g) were shaken with 0.1 M TFA (250ml) in ethanol for 30 minutes. The precipitated Aluminum trifluoroacetylacetate was filtered off [9]

**Chromium Trifluoroacetylacetate.:** Chromic nitrate Nona hydrate (30g) was shaken with acetate buffer (90 cm<sup>3</sup>) and TFA (10 cm<sup>3</sup>) for four hours. The precipitate was air –dried [10]

**Ferric Trifluoroacetylacetate.**

Ferric chloride (2.7 gm) and sodium acetate (5 gm) were shaken with TFA (0.048 gm) in (20 ml) ethanol [11]

**Selenium Piaszelenol**

Equimolar amount of (0.04 M) diamine hydrochloride salt and selenium (IV) as SeO<sub>2</sub> were mixed together in (0.2 M) HCl . The mixture was allowed to stand at room temperature for one hour, the solid piaszelenols were filtered off through a glass-

fiber filter paper and the damp solids recrystallized from 95% ethanol-acetate [12]

The Varian Massspectrometer mode 151 in Baghdad water directorate was used in this study, the mass spectra illustrated below;

## Gas Chromatographic Studies

Stock solution of aluminum, chromium and iron (1000 µg/ml) prepared individually by dissolving known amount of the complexes in toluene. Further dilutions were carried out to prepare standard solution. A good response was obtained for the aluminum and **chromium** complexes using chromatographic conditions and typical chromatogram obtain is shown in Fig. (2). No response was observed from the ECD for the iron complex, but it is suggested that the metal complex decomposed on the Column (13).

Selenium (IV) stock solution (1000 µg/ml) was prepared by dissolving 0.1405 gm of selenium dioxide in 10 ml of concentrated nitric acid and diluted to 100 cm<sup>3</sup> with double distilled water. Working solution were prepared by dilution of stock solution with 5% v/v nitric acid. For the extracted standards 1.00-5.00 µg of Se (IV) were pipettes from 2µg/ml and 1 ml of 0.5% (w/v) the di-amine hydrochloride was added. After standing for two hours, chloropiazselenol were extracted with 25ml of toluene after shaking for five minutes [14]. 5 µl of the sample was injected under the conditions listed in Table {1} and pyunicam gas liquid chromatography mode 133LL was used, the chromatograms obtained is illustrated in Fig.(2).

Table (1) The Gas liquid chromatography Conditions Used for Determination of metals (Al, Cr, Fe and Se) Chelae's

Conditions	Al,Cr,Fe	Se
Column	A glass column chromosorb WAW OV-17, 5% w/v	A glass column chromosorb WAW OV-17, 5% w/v
Temperature	160 C°	130 C°
Carrier gas	Nitrogen	Nitrogen
Detector	63 Ni	63 Ni
Amount injected	3 µl	5 µl

## Determination of Al, Cr, Fe and Se in Water

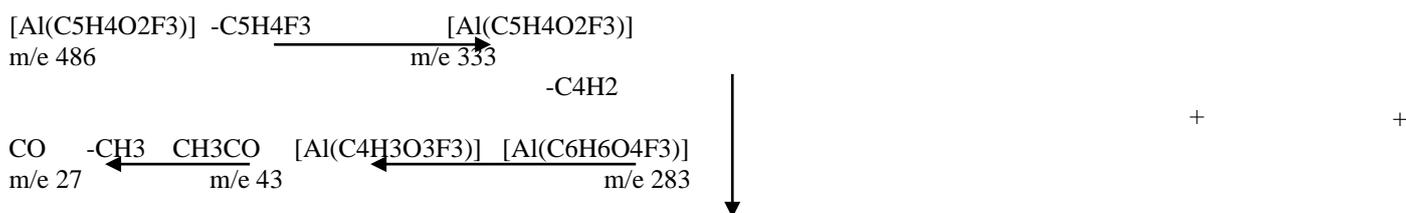
An attempt was carried out to determine aluminum in drinking water in Tikreet city by GLC using solvent extraction method [15], a water sample (1500 ml) was placed in a separating funnel, then 50 ml of acetate buffer was added followed by 0.1M TFA (10ml) in

toluene [16]. The organic layer was washed with 6M NH<sub>4</sub>OH (twice) and diluted to 25cm<sup>3</sup> with toluene. The chromatogram did not show any peaks for aluminum in sample. The same procedure were used for the determination of chromium, again no signal for Cr (III) in the chromatogram

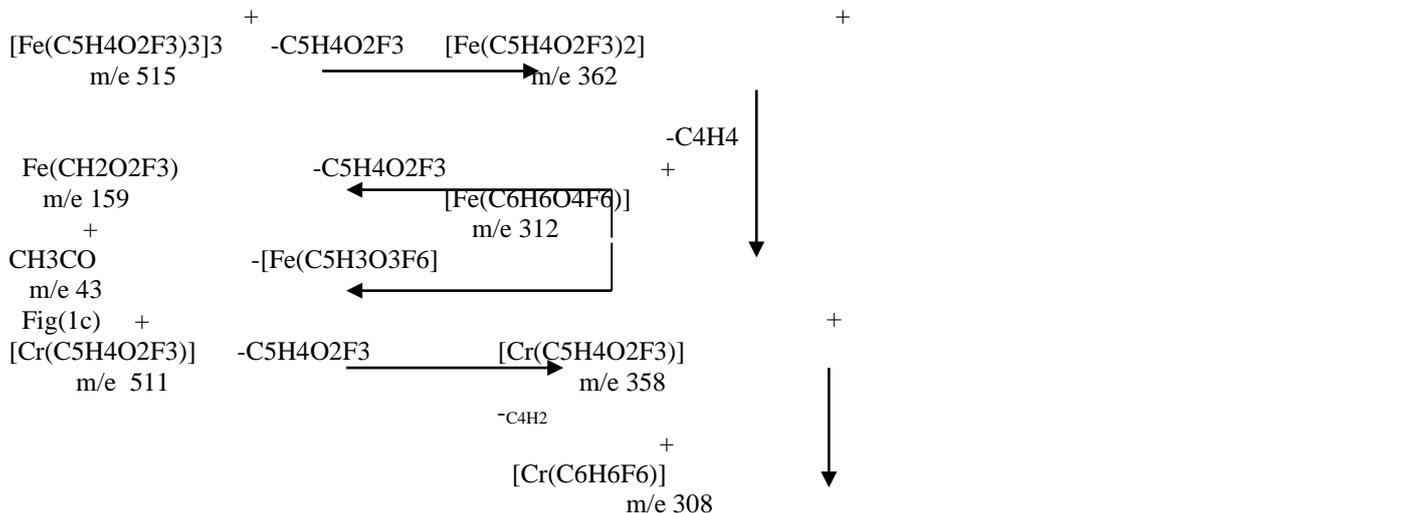
The reduction of Se (VI) to Se (IV) is carried out by heating 1500ml of water sample with mixture of concentrated hydrochloric acid (5 ml) and hydrobromic acid (2.5 ml) by boiling gently for 15 minutes. After cooling to room temperature (2 ml) of 1M NH<sub>2</sub>OH. HCl are added to reduce the excess bromine. The aqueous layer was transferred to flask, (2 ml) of the 0.5% (w/v) 1,2 diamino-4-chlorobenzene were added and the mixture allow to stand for four hours at room temperature, with the aid of 5-10 cm<sup>3</sup> of DDW. The solution was extracted with 10ml of toluene after shaking for five minutes, 5μl of organic phase was injected into gas chromatography with ECD, but no signal for Se(IV) in chromatogram{Fig(3)}.

### **Discussion**

Fig (1) illustrates the molecular weight of metal complexes and the fragmentation pattern as following;(Fig 1a).



Fig( 1b)



Fig(1d)

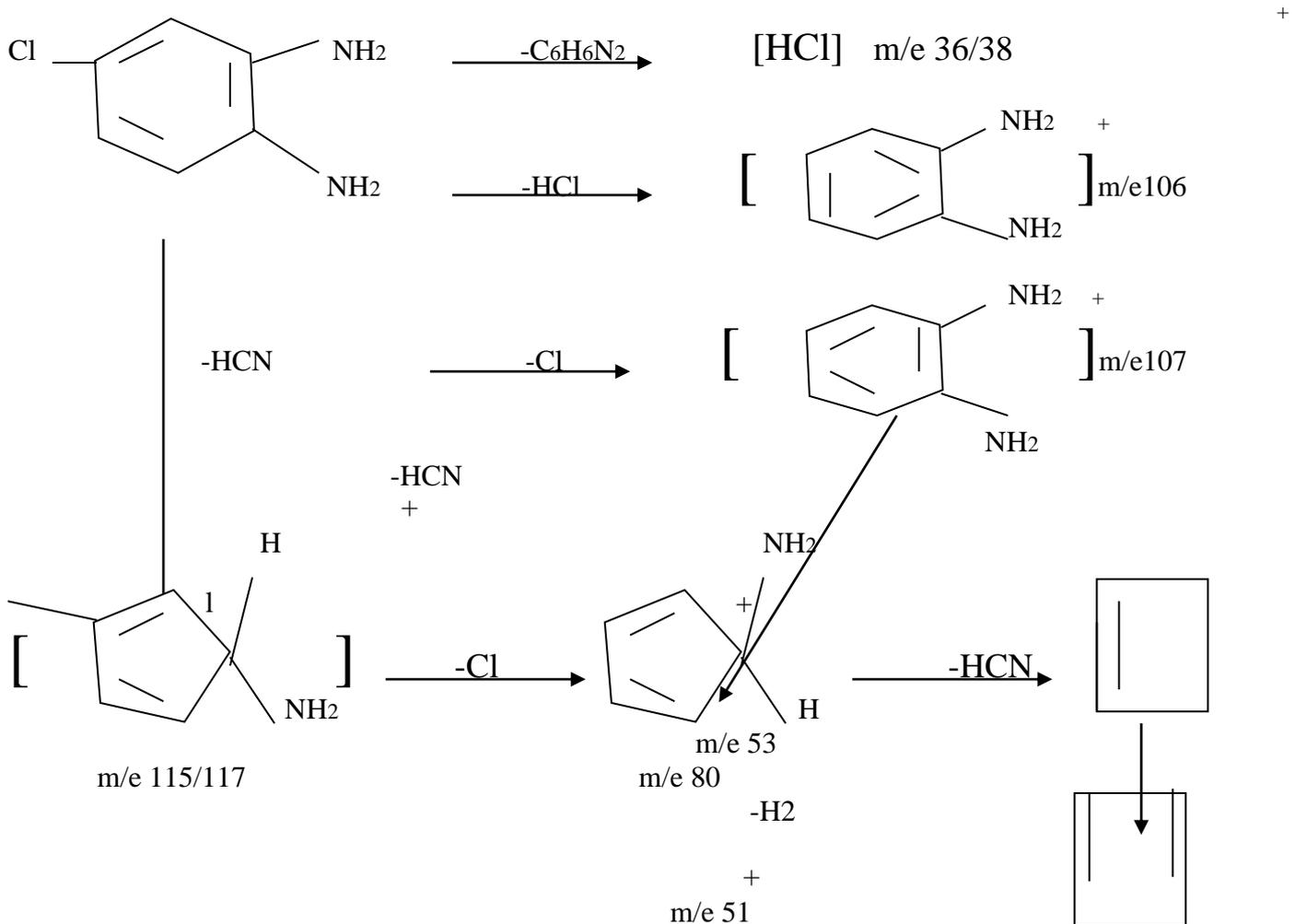


Fig (2a) shows the chromatogram of Al (TFA)<sub>3</sub> as standard solution while aluminum in sample of water was not detected; this indicates that aluminum is precipitated from the samples almost certainly due to the alkaline PH of the solution [17,18]. The chromium can be separated from aluminum and gives greater response Fig (2b). Iron trifluoroacetylacetonate did not give any response, perhaps due to the complexes not being thermally stable at the column temperature, or may be selected experimental conditions were not suitable for the determination of these complexes by GLC [19]

Fig (2c) shows the determination of Al, Cr, Fe and Se(IV) by GLC with ECD, this technique is very sensitive and selective detector for determination of selenium, the piasezenol structure is naturally electron capturing, and introduction of a second electrophori such chloride group in the molecule considerably improves the sensitivity allowing pictogram amount of selenium to be determined [20]

Fig(3) illustrates an attempts for determination of Al,Cr,Fe and Se(IV) in sample water, the results of all samples were the same and showed that the level of these metals in water below their detection limit in this technique. The results obtained in this work agree with other workers (20-25) for determination of aluminum, chromium, iron and selenium (IV) in different matrices.

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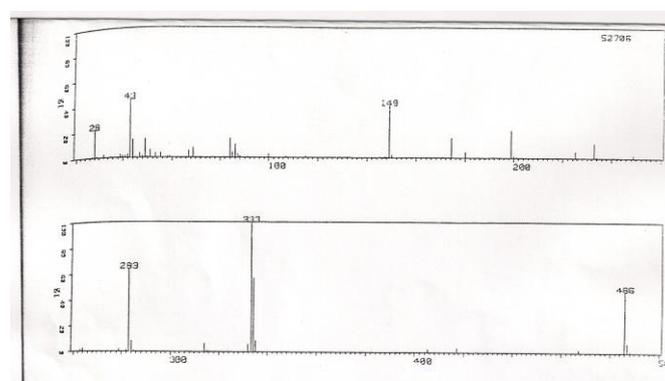


Fig.(1a) Mass Spectrum of Al(TFA)<sub>3</sub>

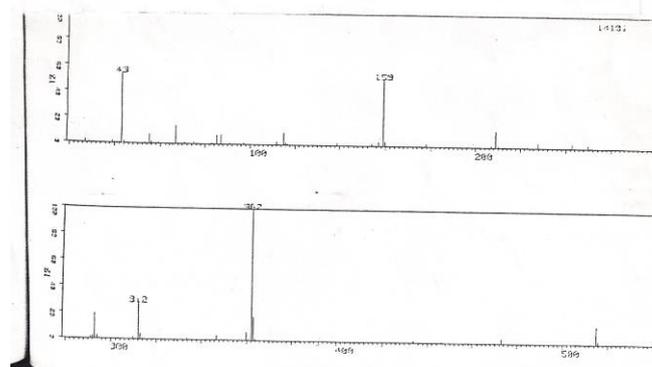


Fig.(1b) Mass Spectrum of Fe(TFA)<sub>3</sub>

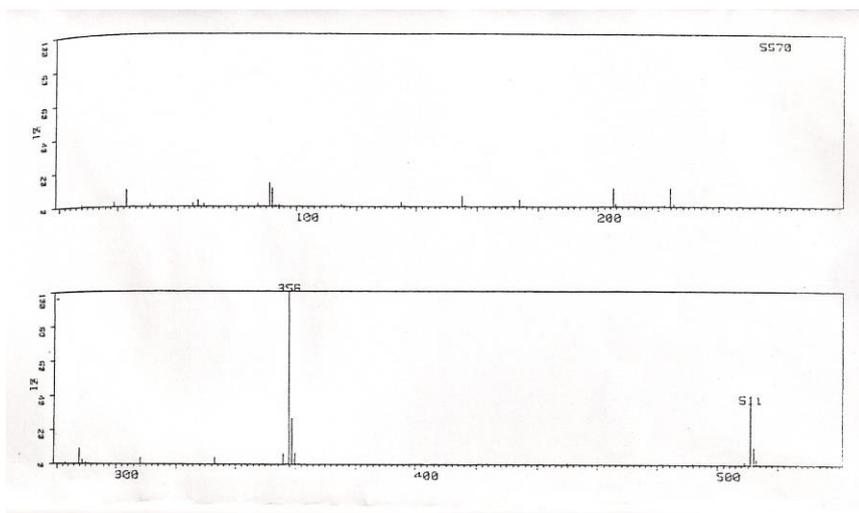
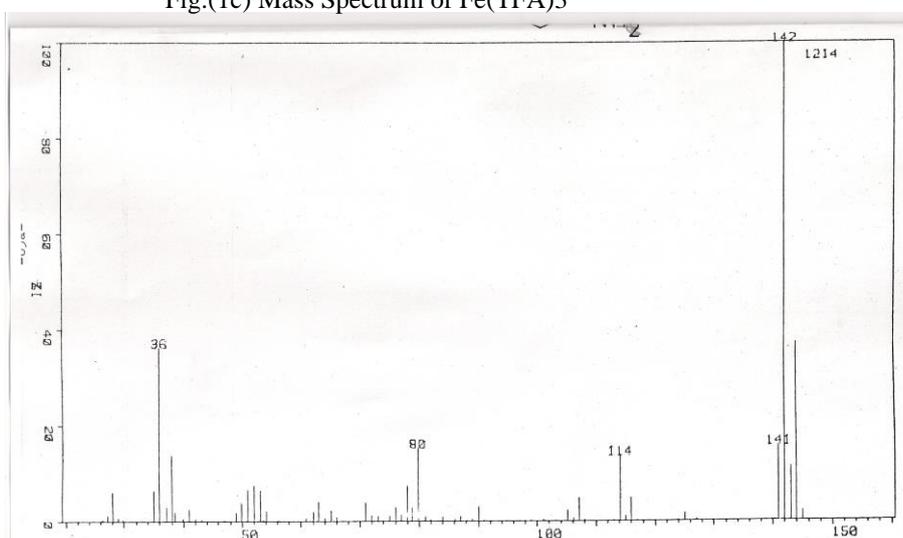
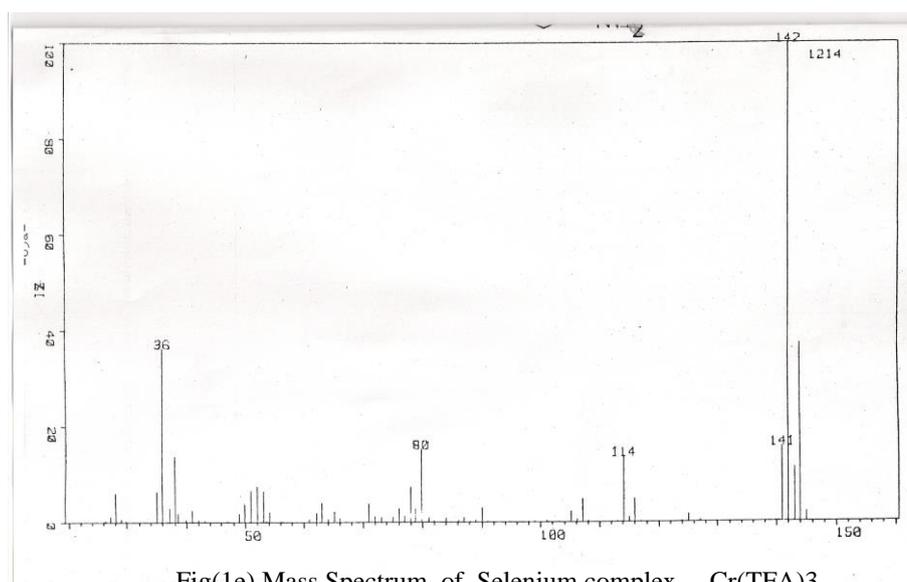


Fig.(1c) Mass Spectrum of Fe(TFA)3



Fig(1d) Mass Spectrum of Selenium complex Cr(TFA)3



Fig(1e) Mass Spectrum of Selenium complex Cr(TFA)3

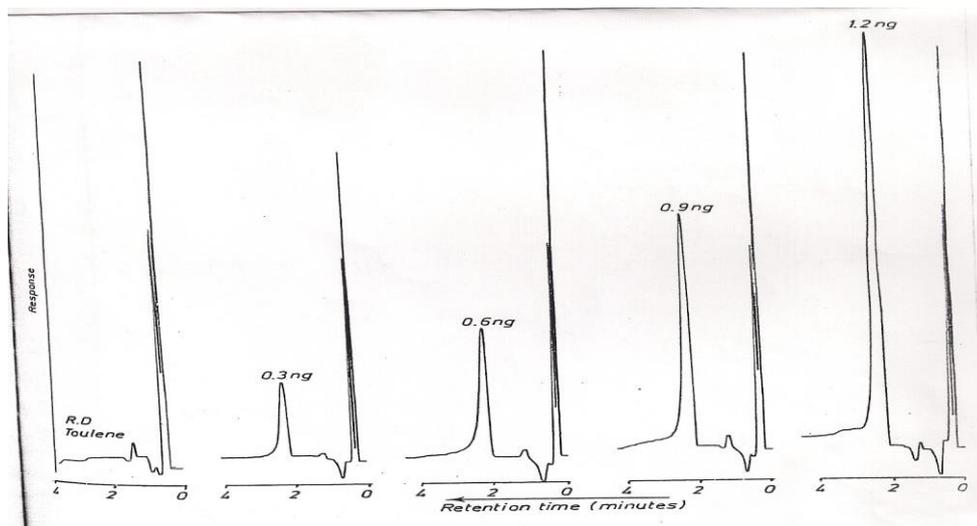


Fig.(2a) Chromatogram of Al(TFA)<sub>3</sub>

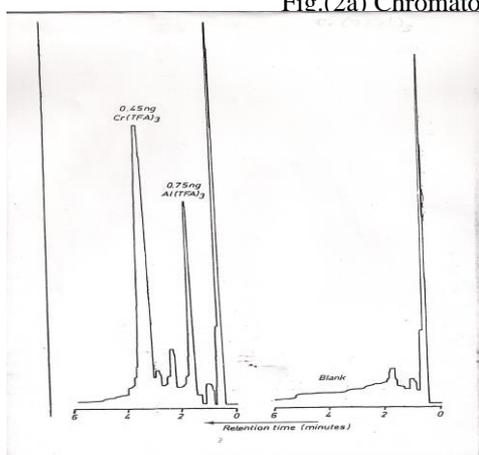


Fig.(2b) Reslution of Al(TFA)<sub>3</sub> and Cr(TFA)<sub>3</sub>

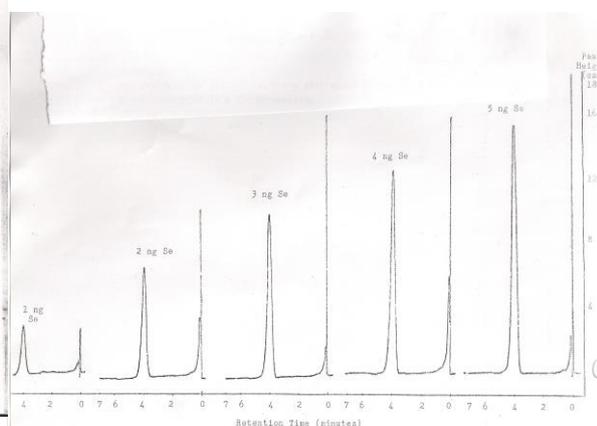


Fig.(2c) Chromatogram of Chloro piazesenol

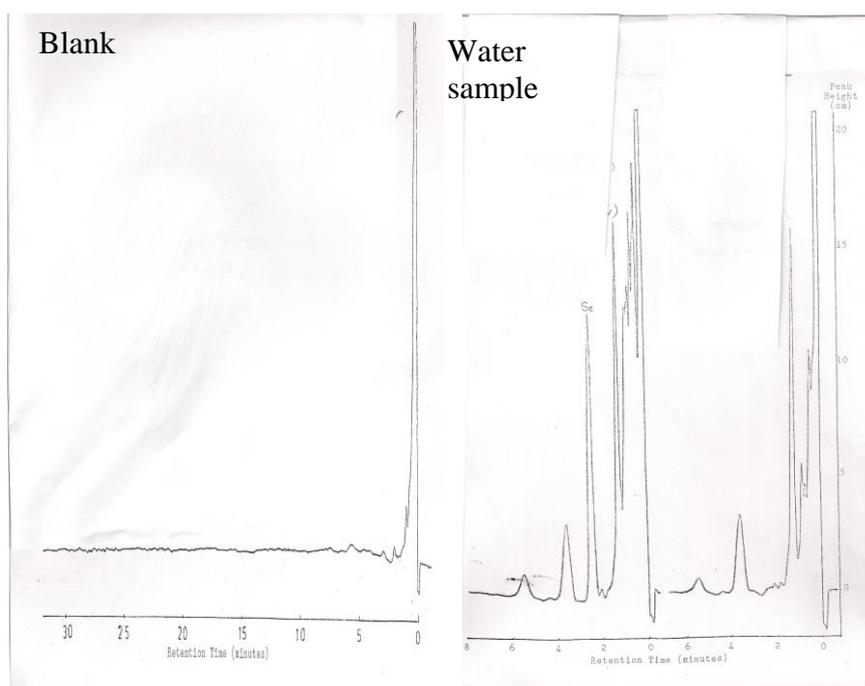


Fig.(3) Chromatogram of Se(IV) in Water

## تقدير معقدات الألمنيوم و الكروم والحديد والسلينيوم في الماء الصالح الشرب لمدينة تكريت بواسطة تقنية كروموتوغرافيا الغازالسائل مع الكاشف الماسك للالكترتون.

حسين حسن خرنوب

### الخلاصة:

تتوفر الامكانية لدى الالمنيوم الثلاثي والكروم الثلاثي بتكوين معقدات مع ثلاثي الفلور لذلك يمكن تقديرها باستخدام تقنية كروموتوغرافيا الغاز مع الكاشف الماسك للأكترونات . تم تطبيق نفس العمليات الكيميائية وتقنيات التحليل للألمنيوم والكروم على عنصر الحديد ولكن لم نحصل على استجابة من قبل الكاشف وهناك صعوبات كثيرة أثناء عملية التحليل. تُعتبر تقنية كروموتوغرافيا الغاز واقعية لتحليل الالمنيوم بسبب امتلاكها دقة في الحساسية ولكنها تحتاج الى وقت لأكمال عملية التحليل. يتحول عنصر السيليونيوم الى 4- كلوروبيزسيتول عند معاملته مع 4-كلور - 1,2 ثنائي الأمين بنزين ويتم استخلاص الأخير من المحلول المائي باستخدام مذيب عضوي (التلوين) لأغراض التحليل بتقنية كروموتوغرافيا الغاز مع الكاشف الماسك للأكترونات ولكن يجب تحويل السيليونيوم السداسي الي سيلينيوم رباعي وذلك باستخدام حامض الهيدروكلوريك المركز او حامض الهيدروبروميك المركز والتسخين لمدة ساعتين عند درجة حرارة 100 م°. وتمتلك تقنية كروموتوغرافيا الغاز مع الكاشف الماسك للأكترونات حساسية عالية لتقدير السيليونيوم قد تصل الى حد  $10^{-12}$  غرام. أجريت محاولات عديدة لتقدير كمية الألمنيوم والكروم والحديد والسلينيوم في عينات ماء صالحة للشرب في مدينة تكريت ولكن بينت النتائج بأن تقنية كروموتوغرافيا الغاز مع الكاشف الماسك للأكترون غير حساسة لهذه العناصر في نماذج المياه.