Gas Chromatography Method for Separation Synthesized Methylethoxysilan Compounds

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Abstract

Modification of gas chromatographic technique for separation methylethoxysilane compounds which were synthesized by the reaction the absolute ethanol with methylchlorosilane compounds. The addition of dry absolute ethanol to methylchlorosilane compounds in the presence of a dry stream of nitrogen gas to eliminate the liberated HCl gas. This method was found to be the suitable method for preparation methylethoxysilane compounds. The optimum parameter selected after careful and precise studies were between 20 – 30 ml \ min to carriers gas flow rate, while applied temperature of detector and injection part are 250 °C and 225 °C respectively. The results showed that suitable chromatographic column for the separation of methylchlorosilane compounds is 50% [5% dioctyl phthalate] + 50% [10% OV- 101] .While 10 % OV – 101 column was found to be the best for the separation of methylethoxysilane compounds . Accordingly , a linear relationship for the calibration curve between concentration and peak area was achieved for methylchlorosilane and methyl ethoxysilane with correlation coefficients were ranged between 0.9991- 1. The results of percentage RSD for the methylchlorosilane and methylethoxysila were 0.51-2.08 and 0.053-1.37 respectively.

Key words: silicon compounds, halosilicon compounds ,methylethylsilicon, gas chromatography.

الخلاصة

اختيرت طريقة كروماتوغرافيا الغاز احدى الطرق التحليليه لفصل وتحليل مركبات مثيل أيثوكسي سايلان المحضرة بدورها من خلال تفاعل الأيثانول المطلق الجاف مع مركبات مثيل كلورو سايلان . ولقد وجد من خلال هذا البحث إن إضافة الأيثانول المطلق إلى مركبات مثيل كلورو سايلان بوجود تيار من غازالنتروجين الذي يعمل على إزاحة غاز HCl المتولد من عملية التفاعل . أنسب الطرق لتحضير هذه المركبات . ثبتت الظروف المثلى و الادق لفصل و تحليل مركبات مثيل ايثوكسي سيلان, حيث تتراوح سرعة الغاز الناقل من 20-30 مل بالدقيقة و بدرجات حرارة المتحسس و غرفة الحقن 250 و 225 درجة مئوية على التوالي. و بينت نتائج التحليل ان أفضل عمود كروماتوغرافي يمكن أستخدامه لفصل وتحليل مركبات مثيل كلورو سايلان هو 50%[5%dioctyl phthalate]+50%[10%OV – 101] أما أفضل عمود لفصل و تحليل مركبات مثيل

أيثوكسي سايلان فكان 10% OV – 101 . تم الحصـــــــــول على علاقة خطية عند عمل منحنى المعايرة بين التركيز والمساحة تحت المنحنى لجميع مركبات مثيل كلوروسايلان ومثيل ايثوكسي سايلان وبمعامل ارتباط (R) تتراوح بين 0.9991 - 1 وقيم RSD% لها بمدى من 0.51-2.08 و1.37-0.53 على التوالي.

Introduction

Silicon element has unique properties in synthesis of organic silicon compounds like alkyl alkoxysiline derivatives. These properties are due to its low value of electronegative, presence of empty d orbital and its big radii comparison with Carbon element[1] Silicon compounds are used as surfaces isolated polymers, cross linking agents and chain initiators[2]. Also silicon has wide uses in industry[3.] Recently silane and siloxane compounds which are containing alkyl or aryl and associated to the silicon directly have great interest in silicon industries field[4.] These compounds are decreased the chemical pollutions through the decreasing of solid waste after the completing of reaction[5.] The chromatography analysis represents one of the most methods which is used in analysis and determination of organic silicon compounds[6.] This technique provided with thermal sensor[7.] Polar or semi polar columns are the best in analysis and separation of these compounds[8-12]. In this paper we report the synthesis of methylethoxysilane from chloromethylsilane with separation and determination of products by using Gas chromatography technique.

Experimental

Instruments

GC type Shimadzu 14 A with thermal conductivity detector (TCD), Data process Apparatus type Shimadzu CR4A, Sensitive Balance A & D 200, Stirring hotplate , Heating mental , Micro syringe , ESSG 10 ml.

Chemicals

All reagents are commercially available and used without further purification.

Columns preparation

Stainless steel columns have been used in separation and analysis of compounds as shown in Table (1)

Chromatography analysis.

1%, 5%, 10%,20%, 30%, 50%,80% and 95% v/v standard solutions of Chloromethylsilane and methyethoxysilane which were prepared by dissolved CCl_4 as a solvent.10 μL from each solution of standard silicon compounds has been injected , after selected the best separation methods in order to determination the retention time of each compounds exactly. Determination optimum conditions by analyzed standard compounds of chloromethylsilan and methylethoxysilan.

Standard calibration curve

A standard calibration graph has been carried out for each study compounds under optimum conditions. The concentrations range 1%-95% v/v were prepared and used to determine the amounts of methylethoxysilan compounds using the method of least squares (MLS) by using the following regression equation[13;]

$Y= Xb+ a$, where Y is the area under peak , x is the calculation unknown concentration , b is the slope.

Calculation the efficiency of chromatographic column

The efficiency of used columns has been calculated through the injection (10 μl) of prepared standard compound solutions in different columns, then The efficiency of all columns has been calculated through the calculation of plate number(n) and length of columns(L) by using the following equation ;

H = L/n , where H is height of plate.

Calculations of thermodynamic functions

The Molar enthalpy and entropy (ΔH and ΔS) were calculated from the graphically relationship between specific retention time and 1/T at deferent temperatures(120-180 C).

Results and discussion

After the preparation of chromatography separation columns, Table (1), and injected 10µL from mixture of standard compounds (chloromethylsilane and methyl ethoxy silane), the results show that the column 50%[5%dioctylphthalate] +50%[10%OV – 101] was the best one for separation of these mixture of compounds, Fig (1). While the column 10%OV – 101 is more suitable for the separation of mixture containing standard methylethoxysilane compounds, Fig (2). The retention time (t_R) is very important in GC specific identification [14.] Its depends on many factors , average gas follow , type of stationary phase, interferences between the substance and stationary phase , column temperature and type of carrier gas. Tables (2) and (3) showed the retention time of the studied compounds on different columns.

Physical properties of chloromethylsilane refer to a closely in range of boiling points between trichloromethylsilane and dichloromethylsilane. This makes their chromatography separation so difficult, because the two compounds have a same kinetic energy on solid support. Also have a closely retention times[15.] Therefore we have concerned on the poor polarity of the two compounds and used high polar stationary phase. Dioctylphthalate was used as a stationary phase due to its high polarity. This phase was effected on adsorption and retention time of the two compounds. Consequently the two compounds have been separated through the inductive phenomenon of polar molecules. We can improve the efficiency of this column by using large mesh size of solid support. On the other hand methylethoxysilane compounds have a wide range deferent in boiling points (25 – 30) C . This is give the chance to separation the two compounds easily on different kinds of columns. But we could not ignore the effect of stationary phase polarity. Where the higher separation efficiency was achieved, when 5% SE – 30 column has been used.

Calculation the efficiency of chromatographic column

The efficiency of all columns has been calculated through the calculation of plate numbers(n) and height of theoretical plate(H). It can be seen from tables (4 '5) shows that the two columns award the best results as well the values of (n) and (H) were 15.7 and 12.3 respectively for the first column, while for the second column were 9.55 and 16.26 respectively.

Calibration Curve

The quantitative analyses of GC depend on the relationship between the concentration of sample and the peak area of the analyzed compound. Table (6) and Fig(4) show straight line equation and association coefficient.

Statistical data of chromatography analysis

The relative standard deviation and recovery of compounds have been calculated . It can seen from table (6) the slightly deviation in accuracy of experimental results comparison with theoretically calculations.

Thermodynamic properties

The net retention volume depends on the amount of stationary phase in column with considering the weight of liquid phase in order to obtain the specific retention volume (Vg) under column temperature, Table (7). The ΔH and ΔS have been calculated from through the graphically relationship of (Vg) against (1/T) with equation followining;[16-17.]

$$\log Vg = \frac{\Delta Hs}{2.303RT} + C^{o} = \frac{\Delta Ss}{2.303RT} + C^{o}$$

where (ΔHs) is partial molar enthalpy and (ΔSs) is partial molar entropy

Practical applications of the suggested analytical method

Preparation method of the compounds which was used in this study gave clear and corresponded results to the standard method, Fig (3) with good yield and without any side products.

Conclusions

The experimental results demonstrate that the column 50%[5% dioctylphalate] + 50%[10%OV-101] is the best one which could used for separation and determination of halosilan compounds and the more suitable column for separation and determination of methylthoxy silan was 10%OV -101.

Modification of gas chromatographic technique have been suitable for the separation and determination of methylethoxysilane compounds products which were synthesized by the addition of absolute ethanol to methylchlorosilane compounds[18] .

Table -1: the preparative columns which were used for separation and analysis of compounds

Liquid phase	Chemical Name	Formula	Support Mesh size	Dimention length X OD
10%SE-30	Dimethyl Poly Siloxane	[(CH3)2SiO]n	Chromosorb 60-80 mesh	2 m X 1/8"
5 % SE-30	=	=	=	=
5 % OV-07	Phenyl methyl + Dimethyl poly – Siloxane	[(ph)CH3SiO]n + [(CH3)2SiO]n	=	=
10% OV-101	Dimethyl Poly Siloxane	[(CH3)2SiO]n	=	1.5 m X 1/4"
5% OV-17	50% phenyl + 50% methyl polysiloxane	[(ph)2SiO]n + [(CH3)2SiO]n	=	2 m X 1/8"
50% [10%ov-101] + 50% [5%dioctyl phthalate]	75% phenyl + 25% alkyl group	[(CH3)2Si-O]n + $[C6H_4\ ]_n$ $(C_7H_{19}COOH)_2$	=	2m X 1/8"

out side diameter = OD

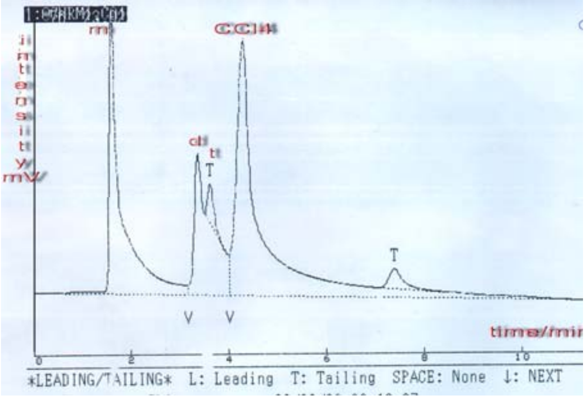

Fig. 1:chromatograph of mixture of t, m and d compounds on column type {50%[10%OV – 101] + 50%[5%dioctyl phthalate] oven programme: int. temp.=35 C○\6 min. rate=5 C○\min.fin. Temp.=60 C○\5 min flow=15ml\min. H

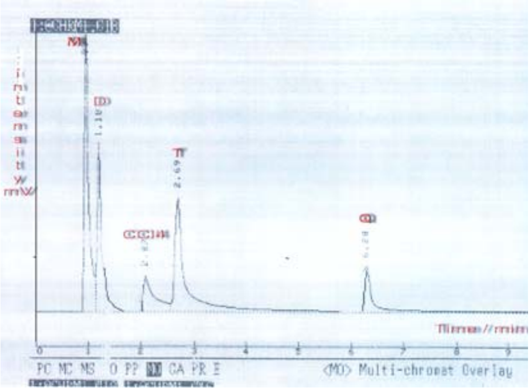

Fig-2: Chromatograph of standard methylethoxysilan compounds mixture on column of 10% OV-101

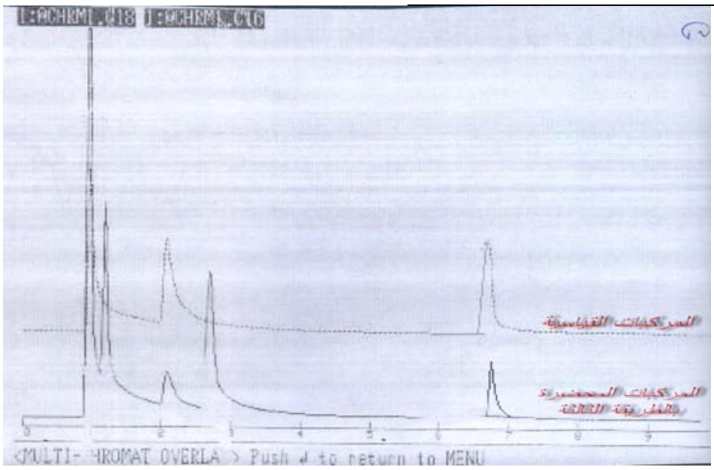

Fig.-3: Comparision of methyjmethoxysilan chromatograph which was synthesized by second method(13) with standard compounds chromatograph .

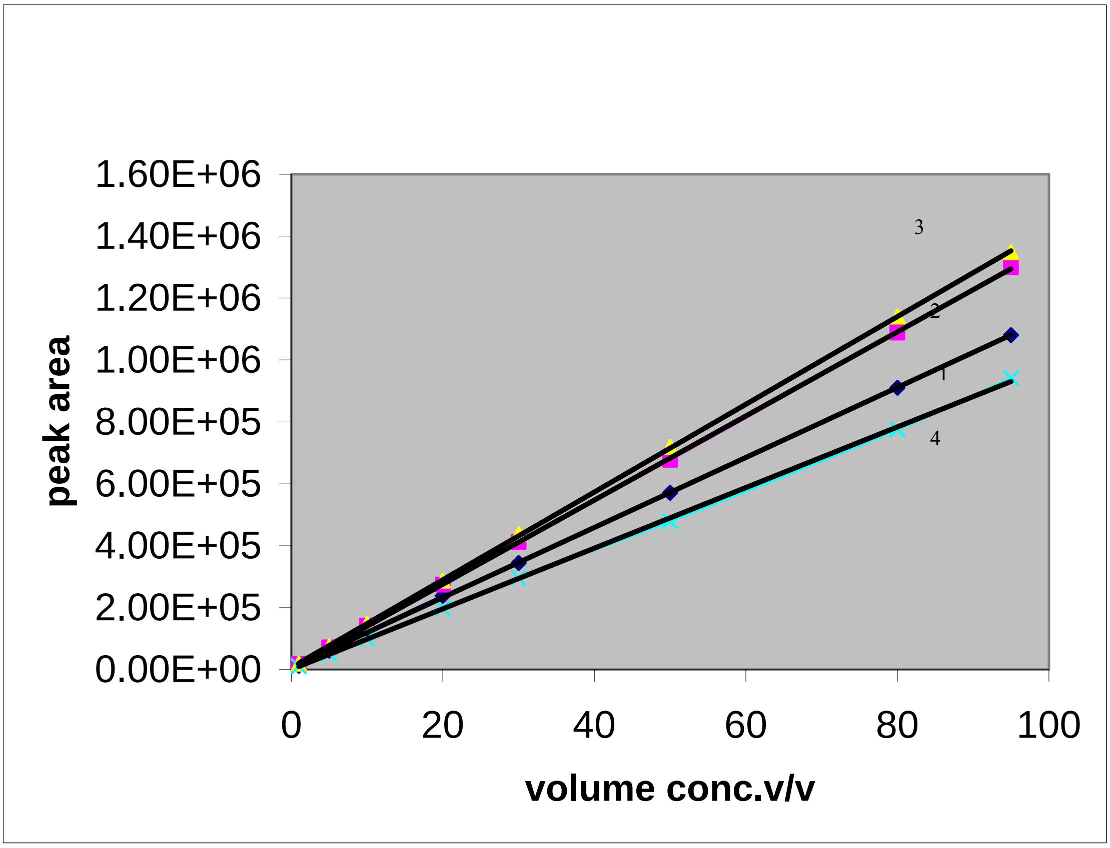

Fig (4) calibration curves of methylethoxysilane compounds on column 10% OV – 101

1- Triethoxy methyl silane .Y = 11310 X + 6116.6 R= 0.9999

2- Diethoxy dimethyl silane .Y = 13596 X + 3271.8 R= 1

3- Monoethoxy trimethyl silane .Y = 14167 X + 6616 R = 1

4- Tetraethoxy silane .Y = 9749.9 X + 131.64 R= 0.9996

Table-2: Retention time of standerd methylchlorosilan compounds on deferent columns

compound	5% SE-30	10% SE-30	10% OV-101	5% OV-7	5% OV-17	5% Dioctyl oven int. T = 45 C	5% Dioctyl oven int. T = 35 C
SiCl4	0.881	1.195	0.867	1.40	0.95	1.57	1.83
(CH3)3SiOC2H5(m)	1.15	1.675	1.15	1.90	2.86	3.57	3.42
(CH3)2Si(OC2H5)2(d)	1.681	2.558	1.717	2.05	6.89	3.84	3.89
CH3Si(OC2H5)3(t)	1.681	2.558	1.717	2.05	6.89	4.61	4.83

Table -3: Retention time value of methylethoxysilan compounds on deferent columns

Compound	10% SE-30	5% SE-30	10% OV-101
(CH3)3SiOC2H5	1.35	2.01	1.10
(CH3)2Si(OC2H5)2	3.56	5.92	2.07
CH3Si(OC2H5)3	11.69	12.76	2.69
Si(OC2H5)4	14.10	17.88	6.28

Table -4: theoretical plate value of methoxyethoxysilan compounds

	10%OV-101	5%SE-30	10%SE-30
n	15.7	14	12.3

Table -5: H value of used columns for separation of methlethoxysilan compounds

	10% OV 101	5%SE-30	10%SE-30
H	9.55	14.28	16.26

Table -6: statistical parameters of methylethoxysilan compounds

Compound	Calc. conc.%	Recovery %	RSD %	Y=bX+a	R
Si(OC2H5)4	9.94	99.44	0.93	Y = 11310 X + 6116.6	0.9999
CH3Si(OC2H5)3(t)	9.97	99.72	1.08	13596 X + 3271.8	1
CH3)2Si(OC2H5)2(d)	9.97	99.71	1.08	14167 X + 6616	1
CH3)3Si(OC2H5)(m)	9.96	99.6	1.09	= 9749.9 X + 131.64	0.9996

Table -7- calculations of – ΔHS and ΔS of methylethoxysilan compounds 1n CCl4 solvent .

Compound	Column 10 % OV-101		Column50%[10%ov-101]50%[5%dioctylpht-halite]	
	- ΔH_S(kj/mole)	ΔS_S(J/k.mole)	- ΔH_S (KJ/mole)	ΔS_S(J/k.mole)
(CH3)3SiOC2H5(m)	17.114	0.675	2.416	6.44
(CH3)2Si(OC2H5)(d)	16.372	0.887	2.748	5.872
CH3Si(OC2H5)3(t)	18.304	1.275	3.191	7.116
Si(OC2H5)4	16.758	1.399	3.335	6.284

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