

# Estimation of Chloride, Sulfate, Sodium, Magnesium and Calcium in Sebacic Acid using Ion Chromatography with Suppressed Conductivity Detection

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**Abstract:** A simple and sensitive ion chromatography (IC) method for the determination of Chloride, Sulfate, Sodium, Magnesium and Calcium from Sebacic acid has been developed and validated. Chloride and Sulfate was separated using high capacity anion exchange column and Sodium, Magnesium and Calcium was separated using cation exchange column. These ions had been analysed by suppressed conductivity detection. For both, anions and cations, linearity of the method has been tested in range of 0.1mg/L to 2.5mg/L, where correlation coefficient observed was >0.999. The limits of detection and quantification have also been established for both, anions and cations. This validated method showed good sensitivity, reproducibility, linearity, specificity and robustness. Therefore, this method can be applicable for routine and regular analysis for anions and cations..

**Keywords:** Sebacic acid, Chloride, Sulfate, Sodium, Magnesium, Calcium, Suppressed Conductivity detection, Ion Chromatography

## 1. Introduction

The demand for household products in India is rising due to increasing customer awareness towards personal hygiene and healthcare. Sebacic acid is one of the main ingredient to manufacture products like cleaning brushes and toothbrushes. Being produced from renewable resources and non-hazardous nature, it is further utilized in manufacturing textiles, automotive, pharmaceuticals, aerospace, cosmetics, candles, plasticizers, hydraulic fluids etc. [1].

Sebacic acid is commercially manufactured from Castor oil. Manufacturing of Sebacic acid from Castor oil is carried out at high temperature like 250°C. [2]. The process involves saponification, acidifications and several water washes to remove acidic and basic impurities. [3]. In Sebacic acid, the presence of common anions (Chloride and Sulfate) and cations (Sodium, Magnesium and Calcium) should be in specified limits, as they directly affect the performance of the finished product in certain application areas. Therefore, identification and quantification of anions and cations in Sebacic acid is of high importance. .

Analytical Chemists utilize combustion Ion Chromatography (CIC) as a tool to determine chloride and sulfate from Sebacic acid type of matrices as it is very difficult to dissolve in water [4]. Though, CIC eases handling of organic matrices for its halides estimation, procuring and operational costs are high and also the methods are tedious. Similarly, cations are estimated using Atomic Absorption Spectroscopy (AAS) or Inductively Coupled Plasma – Optical Emission Spectroscopy or Mass Spectrometry analysis [5]. However, it is altogether different set up and has its own limitations.

The method described in the present article displays advantages in its simplicity and accuracy using conventional Ion chromatography. Both anions and cations can be precisely analysed using methods illustrated herein the article, with ease and economically. .

## 2. Experimental

### 2.1 Reagents and Chemicals

Sebacic acid (industrial grade) was obtained from Jayant Agro-Organics Limited. Analytical Reagent grade reagents and chemicals were used for preparation of reagents, standards and mobile phase. Deionized (DI) water (18.2 MΩ cm, Milli-Q system) and Iso Propyl Alcohol (IPA) in ratio (1 : 1 v/v) was used for the preparation of diluent for standards and samples. DI water was used for preparation of eluent. Sodium Chloride (Merck), Sodium Sulfate (Merck), Magnesium Chloride (Merck), Calcium Chloride (Merck) were used for preparation of standards, Methane sulfonic acid (Merck) was used for the preparation of eluent for cations estimation and RFIC-KOH (Reagent Free Ion Chromatography Potassium Hydroxide) was used for electrolytic generation of Potassium Hydroxide eluent for anions estimation.

### 2.2 Apparatus

The equipment used was Thermo Fisher Dionex Ion Chromatography system ICS Integriion having AS-AP Autosampler with a 50µL loop (for anions analysis) and 25 µL loop (for cations analysis), IonPac AS11-HC, 4mm analytical and IonPac AG11-HC, 4mm guard column along with ADRS600, 4mm was used for anions analysis and IonPac CS17, 4mm and IonPac CG17, 4mm guard column

along with CDRS600, 4mm was used for cations analysis. The experiment was conducted using a pre-degassed DI water and RFIC-KOH for using concentration gradient as given in Table 1 for anions analysis. ADRS600, 4mm suppressor had been used in constant voltage mode with conductivity detection.

**Table 1:** Potassium Hydroxide eluent gradient profile for Standard analysis

Time (minutes)	Flow Rate (mL/min)	Potassium Hydroxide (KOH) mM
0.0	1.50	25.0
15.0	1.50	25.0
15.1	1.50	60.0
20.0	1.50	60.0
20.1	1.50	25.0
25.0	1.50	25.0

Potassium Hydroxide eluent gradient profile for Sample analysis

Time (minutes)	Flow Rate (mL/min)	Potassium Hydroxide (KOH) mM
0.0	1.50	25.0
15.0	1.50	25.0
15.1	1.50	60.0
35.0	1.50	60.0
35.1	1.50	25.0
45.0	1.50	25.0

High concentration of KOH eluent passed through the column for longer period of time to make sure elution of Sebacic acid and to keep the column capacity intact during sample analysis.

Pre-degassed 4mM Methanesulfonic Acid was used as eluent for cations analysis at a flow rate of 1.0mL/min with CDRS600, 4mm in constant voltage mode with Suppressed conductivity detection technique.

Anions and Cations analysis were done separately on Integriion Ion Chromatography system and Software used for data acquisition was Thermo Fisher Dionex Chromeleon (version: 7.2.9). Chromatograms were monitored simultaneously during analysis and results were interpreted.

## 2.3 Procedure

**Preparation of Diluent:** 500mL of DI water is mixed with 500mL of Isopropyl Alcohol (IPA). Sonicated for 10 mins. It was filtered through 0.2 $\mu$  nylon membrane filter and used for analysis.

### For Chloride and Sulfate analysis

**Preparation of Potassium Hydroxide eluent:** - DI water is connected to pump and required concentration (mM of KOH) was generated electrolytically by Reagent Free Ion Chromatography Potassium Hydroxide (RFIC-KOH) module.

**Preparation of standard solutions:** - Certified Sodium Chloride and Sodium Sulfate reagents were procured from

Merck. From these, 1000mg/L Chloride and 1000mg/L Sulfate were prepared in diluent. Table 2 shows concentration of Chloride and Sulfate were prepared in diluent for various parameters of validation study from their 1000mg/L stock.

**Table 2:** Concentration of Chloride and Sulfate used for validation study

Parameter	Chloride mg/L	Sulfate mg/L
Specificity	10.0	10.0
Precision	0.50	0.5
Linearity	0.10, 0.25, 0.50, 1.00 and 2.50	0.10, 0.25, 0.50, 1.00 and 2.50
Limit of Detection (LOD)	0.003	0.007
Limit of Quantification (LOQ)	0.01	0.02

**Sample preparation:** - Weighed accurately 0.25g of Sebacic acid sample in 10mL of volumetric flask, added 6mL of diluent and sonicated for 15 minutes to dissolve and finally made up to the mark with water. Samples were filtered through 0.2 $\mu$  nylon membrane filter and collected in auto sampler vial. This procedure was repeated for each sample along with recovery samples and diluent

### For Sodium, Magnesium and Calcium analysis

**Preparation of 4mM Methanesulfonic Acid:** - 0.27 mL of Methanesulfonic Acid solution was taken in 1000ml volumetric flask containing 500ml of ultrapure deionized water. It was sonicated for 2 minutes and made up to the mark with ultrapure deionized water. It was then filtered through 0.2 $\mu$  nylon membrane filter.

**Preparation of standard solutions:** Certified Sodium Chloride, Magnesium Chloride and Calcium Chloride reagents were procured from Merck. From these, 1000mg/L Sodium, 1000mg/L Magnesium and 1000mg/L Calcium were prepared in diluent. Table 3 shows concentration of Sodium, Magnesium and Calcium were prepared in diluent for various parameters of validation study from their 1000mg/L stock.

**Table 3:** Concentration of Sodium, Magnesium and Calcium used for validation study

Parameter	Sodium mg/L	Magnesium mg/L	Calcium mg/L
Specificity	5.0	5.0	5.0
Precision	0.50	0.50	0.50
Linearity	0.10, 0.25, 0.50, 1.00 and 2.50	0.10, 0.25, 0.50, 1.00 and 2.50	0.10, 0.25, 0.50, 1.00 and 2.50
Limit of Detection (LOD)	0.001	0.008	0.002
Limit of Quantification (LOQ)	0.003	0.026	0.005

**Sample preparation:** - Weighed accurately 0.25g of Sebacic acid sample in 10mL of volumetric flask, added 6mL of diluent and sonicated for 15minutes to dissolve and finally made up to the mark with water. Samples were filtered through 0.2 $\mu$  nylon membrane filter and collected in

auto sampler vial. This procedure was repeated for each sample along with recovery samples and diluent.

An Autosampler (Dionex AS-AP) was used to inject standard solution containing anions or cations into the ion chromatography system. Subsequently, the standard solution in the sample loop was transferred onto the separator column, on which anions or cations were separated. After separation on the column, these ions were detected by Suppressed Conductivity detector. A sequence containing the blank, standards, samples and recovery samples were run and results were then interpreted.

### 3. Results and Discussions

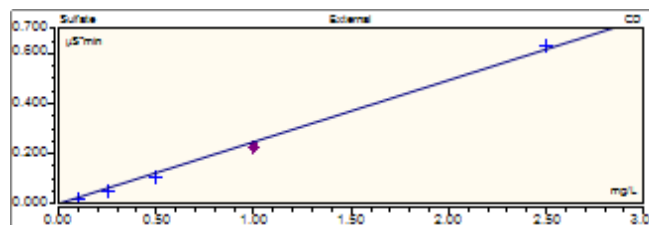
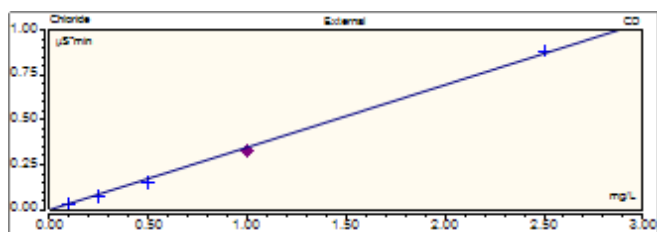
#### For Chloride and Sulfate analysis

Limit of Detection (LOD) for Chloride and Sulfate was 0.003mg/L and 0.007mg/L respectively and injected (n) six times and average signal to noise ratio (S/N) observed was 2.98 for Chloride and 3.10 for Sulfate. Limit of Quantification (LOQ) for Chloride and Sulfate was 0.01mg/L and 0.02mg/L respectively, it was injected (n) six times and observed signal to noise ratio (S/N) was 9.95 for Chloride and 10.11 for Sulfate. Its percent relative standard deviation (RSD) for peak area was 1.90% for Chloride and 1.81% for Sulfate respectively. Table 4 shows results for LOD and LOQ of Chloride and Sulfate.

**Table 4:** LOD and LOQ data for Chloride and Sulfate

Chloride			
Parameter	Amount, mg/L	S/N	% RSD (n=6)
LOD	0.003	2.98	Not Applicable
LOQ	0.01	9.95	1.90%
Sulfate			
Parameter	Amount, mg/L	S/N	% RSD (n=6)
LOD	0.007	3.10	Not Applicable
LOQ	0.02	10.11	1.81%

The response of the analytes was linear over the range of 0.1 to 2.5mg/L for both chloride and sulfate. Calibration curve fits well and that is significantly linear having correlation coefficient of 0.9996, slope 0.3475 and offset 0.00 (figure 1) for Chloride and correlation coefficient of 0.9991, slope 0.2474 and offset 0.00 (figure 1) for Sulfate. This linearity study was performed for the concentration range of 0.10, 0.25, 0.50, 1.00 and 2.50mg/L of both Chloride and Sulfate. Each standard injection was repeated thrice. Therefore, number of calibration points (n) for linearity study was 15. Its data had been shown in table 5.



**Figure 1:** Linearity plot for Chloride and Sulfate.

**Table 5:** Linearity data for Chloride and Sulfate

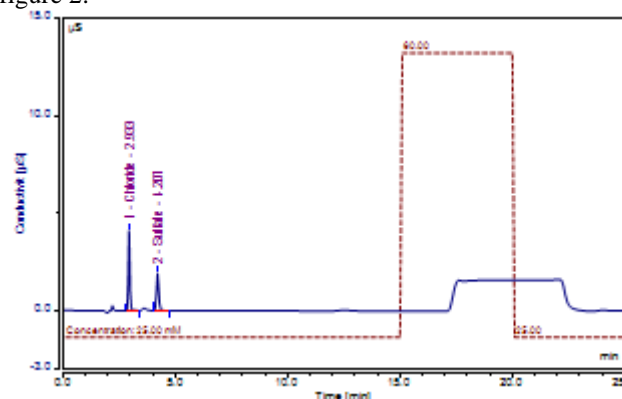
Analyte	Points	Corr. Coeff.	Offset	Slope
Chloride	15	0.9996	0	0.3475
Sulfate	15	0.9991	0	0.2474

Replicate injections mixture of chloride and sulfate standard was done and it's percent relative standard deviation for peak area was 0.98% for chloride and 1.13% for Sulfate respectively. Table 6 shows results for their precision study.

**Table 6:** Precision data for Chloride and Sulfate

Analyte	Amount, mg/L	% RSD (n=10)	Resolution (USP)
Chloride	0.50	0.98	8.40
Sulfate	0.50	1.13	Not Applicable

Chromatogram for chloride and sulfate standard is shown in figure 2.



**Figure 2:** Standard chromatogram for Chloride (1.0mg/L) and Sulfate (1.0mg/L)

**Sample results:** - Samples were analysed using the linearity calibration method. Replicate injections of same sample was also done. Its results and routine analysis sample results were shown in table 7 and table 8. Sample chromatogram was shown in figure 3.

**Table 7:** Sample precision

Analyte	B. No.	Number of injections	% RSD
Chloride	G18-58	10.0	0.69
Sulfate	G18-58	10.0	0.74

**Table 8:** Routine sample analysis results

B. No.	Chloride mg/Kg	Sulfate mg/Kg
G18-58	2.86	6.77
G18-943	Not Detected	55.80
G18-936	17.17	55.09
F1-10	23.88	5.24
F1-28	21.01	4.88

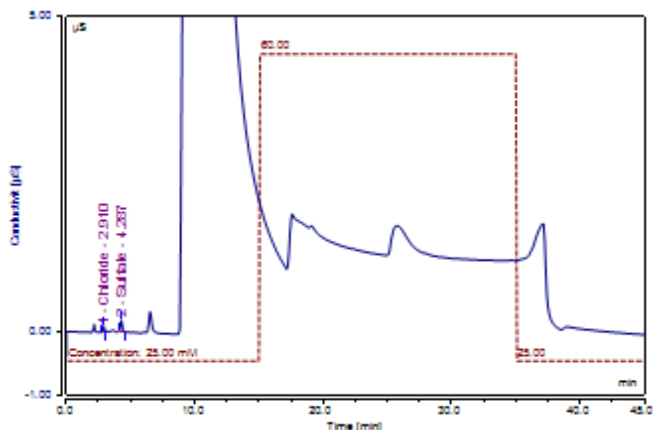


Figure 3: Sample chromatogram for Chloride and Sulfate estimation (B. No. G18-58).

**Recovery:** - The sample used for recovery study was B. No. G18-58 (average concentration was taken for calculation). Recovery test solutions were injected in triplicate Also for recovery study, known concentrations of amount was added to sample at three different levels as shown in table 9.

Table 9: Recovery study (Chloride and Sulfate) for sample (B.No. G18-58) (n = 3) (Required quantity of IPA is added to make sample in solubilized state)

Analyte	Target Concentration	Amount Added, mg/L	Amount Recovered, mg/L	% Recovery
Chloride	50%	0.250	0.255	102.0
	100%	0.500	0.486	97.2
	150%	0.750	0.760	101.3

Analyte	Target Concentration	Amount Added mg/L	Amount Recovered mg/L	% Recovery
Sulfate	50%	0.250	0.240	96.0
	100%	0.500	0.491	98.2
	150%	0.750	0.758	101.1

**Method Ruggedness:** - Method was tested with different flow rate like 1.3 and 1.7. Also, it was tested using different eluent concentrations. Method was proven to be rugged as it does not show any changes in sample results due to changes in flow rate or eluent concentration.

**For Sodium, Magnesium and Calcium analysis**

Limit of Detection (LOD) for Sodium, Magnesium and Calcium was 0.001mg/L, 0.008mg/L and 0.002mg/L respectively and injected (n) six times and observed average signal to noise ratio (S/N) was 3.12 for Sodium, 2.95 for Magnesium and 2.91 for Calcium. Limit of Quantification (LOQ) for Sodium, Magnesium and Calcium was 0.003mg/L, 0.026mg/L and 0.005mg/L respectively, it was injected (n) six times and observed signal to noise ratio (S/N) was 10.98 for Sodium, 9.94 for Magnesium and 9.97 for Calcium.. It's percent relative standard deviation for peak area was 1.19% for Sodium, 1.43 for Magnesium and 1.51% for Calcium respectively. Table 10 shows results for LOD and LOQ of Sodium, Magnesium and Calcium.

Table 10: LOD and LOQ data for Sodium, Magnesium and Calcium

Sodium			
Parameter	Amount, mg/L	S/N	% RSD (n=6)
LOD	0.001	3.12	Not Applicable
LOQ	0.003	10.98	1.19%
Magnesium			
Parameter	Amount, mg/L	S/N	% RSD (n=6)
LOD	0.008	2.95	Not Applicable
LOQ	0.026	9.94	1.43%
Calcium			
Parameter	Amount, mg/L	S/N	% RSD (n=6)
LOD	0.002	2.91	Not Applicable
LOQ	0.005	9.97	1.51%

The response of the analytes was linear over the range of 0.1 to 2.5mg/L for each of Sodium, Magnesium and Calcium. Calibration curve fits well and that is significantly linear having correlation coefficient of 0.9992, slope 2.7874 and offset 0.00 (figure 4) for Sodium, correlation coefficient of 0.9999, slope 4.6923 and offset 0.00 (figure 4) for Magnesium and correlation coefficient of 0.9999, slope 1.8615 and offset 0.00 (figure 4) for Calcium. This linearity study was performed for the concentration range of 0.10, 0.25, 0.50, 1.00 and 2.50mg/L of each of Sodium, Magnesium and Calcium. Each standard injection was repeated thrice. Therefore, number of calibration points (n) for linearity study was 15. Its data had been shown in table 11.

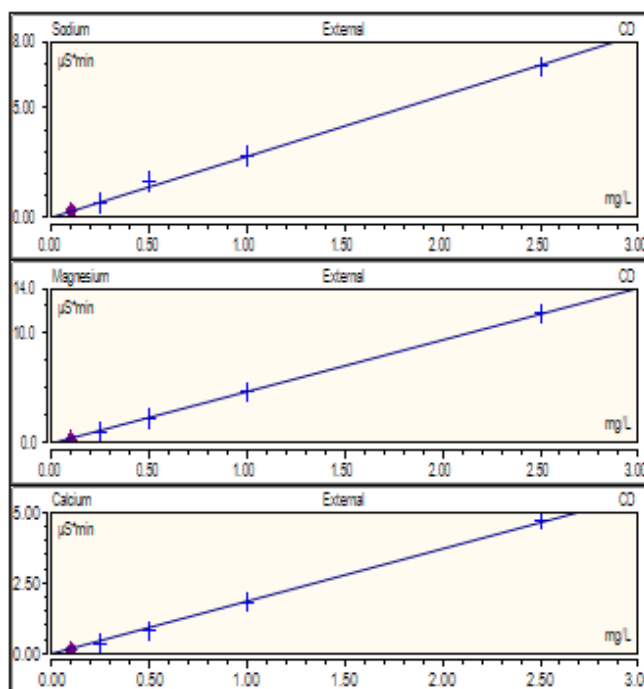


Figure 4: Linearity plot for Sodium, Magnesium and Calcium.

Table 11: Linearity data for Sodium, Magnesium and Calcium

Analyte	Points	Corr. Coeff.	Offset	Slope
Sodium	15	0.9992	0	2.7874
Magnesium	15	0.9999	0	4.6923
Calcium	15	0.9999	0	1.8615

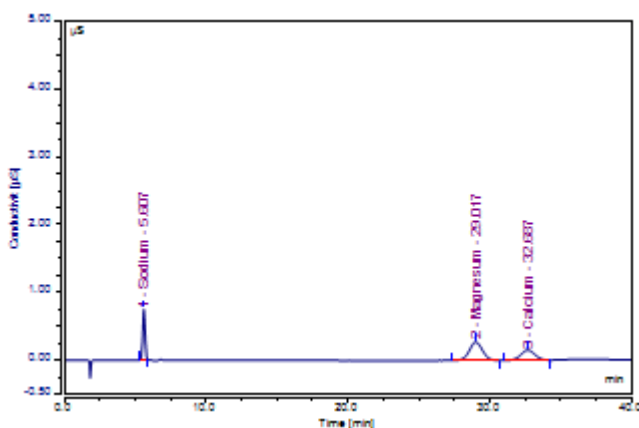


Replicate injections mixture of Sodium, Magnesium and Calcium standards was done and its percent relative standard deviation for peak area was 0.82% for Sodium, 0.95% for Magnesium and 1.05% for Calcium respectively. Table 12 shows results for their precision study.

**Table 12:** Precision data for Sodium, Magnesium and Calcium

Analyte	Amount, mg/L	% RSD (n=10)	Resolution, (USP)
Sodium	0.50	0.82	24.22
Magnesium	0.50	0.95	2.18
Calcium	0.5	1.05	Not Applicable

Chromatogram for Sodium, Magnesium and Calcium standard is shown in figure 5.



**Figure 5:** Standard chromatogram for Sodium (1.0mg/L), Magnesium (1.0mg/L) and Calcium (1.0mg/L)

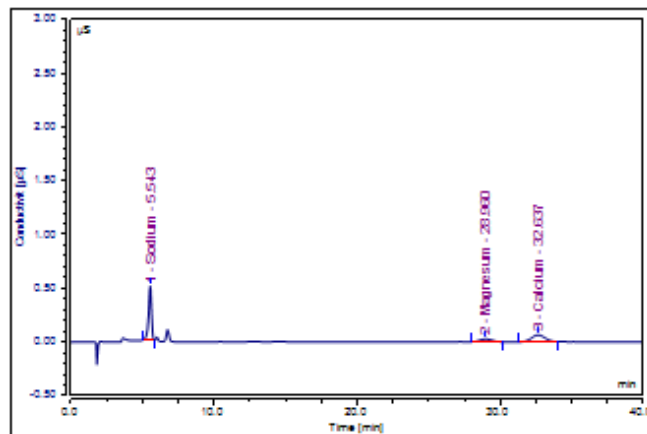
**Sample results:** - Samples were analysed using the linearity calibration method. Replicate injections of same sample was also done. Its results and routine analysis sample results were shown in table 13 and table 14. Sample chromatogram was shown in figure 6.

**Table 13:** Sample precision

Analyte	B. No.	Number of injections	% RSD
Sodium	G18-58	10.0	0.88
Magnesium	G18-58	10.0	0.73
Calcium	G18-58	10.0	1.01

**Table 14:** Routine sample analysis results

B. No.	Sodium mg/Kg	Magnesium mg/Kg	Calcium mg/Kg
G18-58	27.13	Not Detected	3.56
G18-943	30.41	2.27	14.69
G18-936	21.89	Not Detected	12.05
F1-10	25.14	1.66	17.50
F1-28	23.98	1.51	17.63



**Figure 6:** Sample chromatogram for Sodium, Magnesium and Calcium estimation (B. No. G18-943)

**Recovery:** - The sample used for recovery study was sebacic acid, B. No. G18-58 (average concentration was taken for calculation). Recovery test solutions were injected in triplicate Also for recovery study, known concentrations of amount was added to sample at three different levels as shown in table 15.

**Table 15:** Recovery study (Sodium, Magnesium and Calcium) for sample (B.No. G18-58) (n = 3) (Required quantity of IPA is added to make sample in solubilized state)

Analyte	Target Concentration	Amount Added mg/L	Amount Recovered mg/L	% Recovery
Sodium	50%	0.250	0.263	105.2
	100%	0.500	0.515	103.0
	150%	0.750	0.755	100.7

Analyte	Target Concentration	Amount Added mg/L	Amount Recovered mg/L	% Recovery
Magnesium	50%	0.250	0.244	97.6
	100%	0.500	0.487	97.4
	150%	0.750	0.753	100.4

Analyte	Target Concentration	Amount Added mg/L	Amount Recovered mg/L	% Recovery
Calcium	50%	0.250	0.258	103.2
	100%	0.500	0.503	100.6
	150%	0.750	0.760	101.3

**Method Ruggedness:** Method was tested with different flow rate like 0.8 and 1.2. Also, it was tested using different eluent concentrations. Method was proven to be efficient as it does not show any changes in sample results due to changes in flow rate or eluent concentration.

#### 4. Conclusions

In the present work, an Ion Chromatography Suppressed Conductivity Detection method was validated and successfully used to provide qualitative and quantitative analysis of Chloride, Sulfate, Sodium, Magnesium and Calcium in Sebacic Acid samples. This technique is proven to be efficient and cost effective with respect to analysis

required for keeping check on its limit of Chloride, Sulfate, Sodium, Magnesium and Calcium in Sebacic Acid by using reagent free ion chromatography.

Reagent free ion chromatography provides ease of use with electrolytic generation of eluent. This technology provides feasibility of gradient and isocratic analysis from Sebacic acid.

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## Author Profile



**Chetan Chavan** had completed B.Sc (Chemistry). and M.Sc (Chemistry) from Mumbai University and completed his Ph.D in year, 2018., He had joined Dionex India Pvt. Limited, which is now Thermo Fisher Scientific Pvt. Ltd., as Applications Manger for Ion Chromatography (IC) and HPLC and currently working as Product Manager – IC/SP. His role is to provide technical support coordination with factory for India team requirements, provide guidance to sales, application and service team for IC and HPLC.



**Chanakya Thaker** received B. Sc (Chemistry). and M.Sc (Analytical Chemistry) from Mumbai University in 2006 and 2008, respectively. From 2009, he had joined Dionex India Pvt. Limited, which is now Thermo Fisher Scientific Pvt. Ltd., as Applications Specialist for Ion Chromatography (IC) and HPLC and currently working as Applications Manager – IC/SP. His role is to manage application team, provide customer training, sample analysis, technical presentations, method development and troubleshooting on IC and HPLC systems.



**Chetan Chaudhari** received B. Pharm. and M. Pharm from Mumbai University in 2008 and 2010, respectively. From 2015, he had joined Fisher Scientific Pvt. Ltd., as Applications Specialist for Ion Chromatography (IC) His role is to provide customer training, sample analysis, method development and troubleshooting on IC systems.



**Subhash Udeshi** has completed his Ph.D (Chemical Engineering) Rutgers University, New Jersey, USA in 1987. At present, he is Director of Jayant Agro-Organics Ltd. Working in castor oil industry since 30 years. Developed New Products and Processes for Polyols, Resins, Nylon-11, Sebacic Acid, 2-Octanol, Metallic Salts of Fatty Acids, Refining, Dimer Acid, Distillation, Pyrolysis, Hydrogenation, Plasticizers. Developed QC-methods for various products and intermediates obtained during the processing. Was Co-Principal Investigator, "Value Chain on Castor & Its Industrial Products", under National Agricultural Innovation Project (NAIP) sponsored by World Bank through Indian Council of Agricultural Research, Ministry of Agriculture, Government of India – 2009 to 2012.