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DEVELOPMENT OF METHOD FOR DETERMINATION OF SODIUM MONOCHLOROACETATE AND SODIUM DICHLOROACETATE IN COCOAMIDO PROPYL BETAINE BY GAS CHROMATOGRAPHY: FID, ECD AND MS

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ABSTRACT

Cocoamide Propyl Betaine is a feedstock for consumer products of cosmetic and household segments. Sodium monochloroacetate and sodium dichloroacetate impurities are toxic, irritating and harmful to the environment and lower concentrations - parts per million level - are required in process control of producers and regulatory affairs. Regarding analytical test method, two conditions should be met: quantification limit, precision and accuracy should be appropriate; different techniques for gas chromatography - ECD, FID and MS - should be available, since for manufacturer is not so easy to keep electron capture detector by radioactive source Ni 63 due to government control and need of qualified radiological protection. The samples are obtained at manufacturers; for the analyte separation, treatment methodologies are employed by liquid-liquid extraction and solid phase extraction. Alternative detectors used in this study are: Flame Ionization and Mass Spectrometer with Electron Ionization. The validation process will be applied to methodology to ensure a selective, robust, accurate and reproducible analytical determination.

1. INTRODUCTION

Surfactants or tensides are a class of chemical products used in industry that dissolved in water reduce surface tension (liquid-liquid), or interfacial tension (liquid-solid) [1]. Although having variable composition, the surfactants have a common characteristic that the molecular structure contains a hydrophobic component and the other hydrophilic, such that once dissolved in water, the hydrophilic ends are directed to water and to hydrophobic another phase. If the other phase is dirt, it will be surround by a surfactant film, promoting the formation of a micelle that is released from the substrate to be cleaned [2].

Surfactants are used in a wide range of chemical processes – oil, emulsions, pharmaceutical, food and personal care - because their properties enable them to act as emulsifying, wetting, dispersing and foaming[3]. The classification regarding to electrical charge of functional groups is performed as follows: cationic, anionic, non-ionic and amphoteric [4].

Within this latter class of surfactants, the amphoteric betaines consist of a carboxylate or sulfonate group and a quaternary nitrogen group. The properties such as solubility, detergency, foaming and wetting power of surfactants of this class are mainly conditioned to pH of the medium and the length of the carbonic chain.

The cocoamidopropyl betaine is obtained by condensation of coconut fatty acid with dimethylaminopropylamine and subsequent reaction with monochloroacetic acid as the following equations 1 and 2 [5]:

1st Step: condensation of coconut fatty acid with dimethylaminopropylamine:

$$CH_3(CH_2)_{10}COOH + H_2CH_2CH_2CH_2N(CH_3)_2 \rightarrow CH_3(CH_2)_{10}C(O)N(H)CH_2CH_2CH_2N(CH_3)_2 + H_2O \quad (1)$$

2nd Step: reaction of amidoamine from 1st Step with monochloroacetic acid:

$$CH_3(CH_2)_{10}C(O)N(H)CH_2CH_2CH_2N(CH_3)_2 + ClCH_2CO_2H + NaOH \rightarrow CH_3(CH_2)_{10}C(O)N(H)CH_2CH_2CH_2N^+(CH_3)_2CH_2CO_2^- + NaCl + H_2O \quad (2)$$

Since it is compatible with all class of surfactants, cocoamidopropyl betaine is applied in a wide range of formulations intended for personal care and home care since the 60's and is recognized as oily particulate dirt remover, foam stabilizer, good stability in a wide pH range and lower skin and eye irritant than the anionic surfactants, as reported in the technical literature from manufacturers [6].

The constituents of CAPB with applicative function are Cocoamido,N-[(3-dimethylamine) propyl], betaine (active matter), Cocoamido, N-[(3-dimethylamine) propyl] (residual intermediate) and Sodium Chloride (by-product) [7]. Impurities are Sodium Monochloroacetate (raw material), Sodium Dichloroacetate (raw material), Dimethylamino Propylamine (raw material) and Sodium Glycolate (by-product).

The impurities Sodium Monochloroacetate (MCAS) and Sodium Dichloroacetate (DCAS) have toxic and irritant effects, as the safety data sheets of the manufacturers and the literature [8, 9] and strict controls are required - maximum level 30 mg/kg - depending on the application, region, market and regulatory affairs.

The detection mode by electron capture (ECD) is used in the chemical industry, however, there are disadvantages: this detector contains radioactive ^{63}Ni and companies are required to provide CNEN (Comissão Nacional de Energia Nuclear) license to use equipment with radioactive material; qualified people in radiation protection is need; the use of ECD detector is restrict because it is less universal than mass spectrometry (MS) due to selectivity to functional groups with electronegative elements [10].

The development of alternatives in gas chromatography to determine chloroacetic acid in amphoteric through the detection mode MS is relevant due to the levels of detectability and universal response [10].

Through metrological requirements that ensure the reliability of each of the techniques, the user can adopt a particular test method, considering the availability of technology and equipment, response time and robustness for quality control [11].

2. OBJECTIVE

The scope of this work is to develop analytical methods for determination of sodium monochloroacetate (MCAS) and sodium dichloroacetate (DCAS) by gas chromatography with electron capture detection GC/ECD and mass spectrometry detection GC/MS, in process control and final inspection of Cocoamido Propyl Betaine (CAPB).

3. METHODOLOGY

The samples of CAPB were get from producers and any sample is representative of an industrial batch, with common and uniform characteristics and identified unequivocally.

This study used common reagents and ordinary laboratory apparatus. The chromatographs used were GC/ECD Agilent 6890N or Shimadzu GC-17A and GC/MS Shimadzu QP2010, both with split/splitless injector.

The determination of MCAS and DCAS in CAPB consists of two steps:

- preparation of the sample for chromatographic injection, that contemplates derivatization of the analytes to more volatile compounds – MCAS and DCAS are esterified with ethanol in acidic medium – and matrix purification operations, which minimize interference and optimize the analyte signal [12, 13].

- the chromatographic determination, that performs the separation (qualitative parameter is retention time) and quantification (parameter is peak area which is proportional to the concentration of the component in the sample) of volatile compounds [14].

The MCAS and DCAS determinations in CAPB by ethanol esterification is based on:

- methanol esterification, headspace technique, detection by ECD [15]
- derivatization to their propyl-esters with ECD detection [16]
- derivatization with sulfuric acid and ethanol is conducted with liquid-liquid or solid phase extraction with detection by MS [17]

4. EVALUATION OF RESULTS

This section presents the qualitative and quantitative results of the MCAS and DCAS standards and their determinations in CAPB matrix.

4.1. Derivatization of the analytes and extraction from matrix CAPB

The initial tests converting Chloroacetic Acid standards in Esters were carried out with Ethanol 96% and temperature 85°C for 20 minutes; there was absence of characteristic peaks in the chromatograms of MCAS and DCAS standards, confirming the necessity of using anhydrous alcohols and temperatures 100°C [18]. In the other experiments with Absolute Ethanol, were

observed oven temperatures up to 115°C, the samples became dark and there was no chromatographic response, indicating the degradation of esterified compounds; to solve the problem of not stabilizing the temperature, it is adapted in the laboratory an oven with electronic temperature controller.

At the first tests involving extraction with hexane was used manual stirring instead of magnetic stirring, also observed loss of response to the analytes and it was standardized the magnetic agitation.

In order to achieve better resolution in the MS detection, was employed butanol as esterifying agent, in substitution to ethanol, expecting to get gain in response with a higher number of carbons, however, there was loss in resolution. Figure 1 presents GC/MS profiles: in the esterification with ethanol the peaks present appropriate resolution, MCAS at 5.5 minutes and DCAS 7.5 minutes (top chromatogram); in the esterification with butanol, MCAS and DCAS peaks were unified at 6.7 minutes (bottom figure).

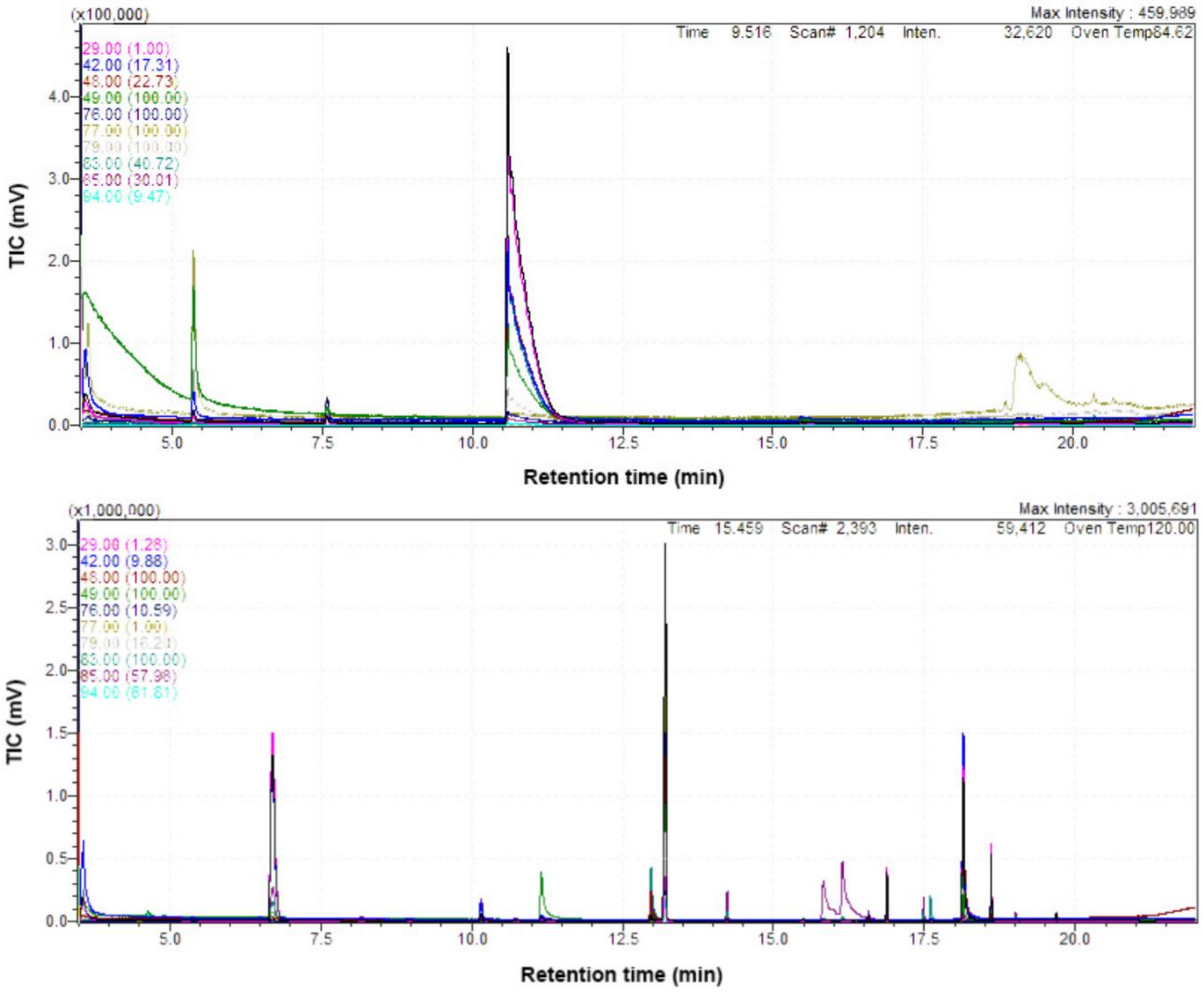

Figure 1: Chromatographic profiles in GC / MS mode "Selected Ion Monitoring SIM" for MCAS 24 mg/kg and DCAS 44 mg/kg esterified with ethanol (upper) and butanol (lower)

The preparation and determination in quadruplicate of standards MCAS 72 mg/kg and DCAS 66 mg/kg pointed out significant differences in the chromatographic profiles by GC/MS, as can be seen in Figure 2, confirming the need to improve control of the sample preparation conditions.

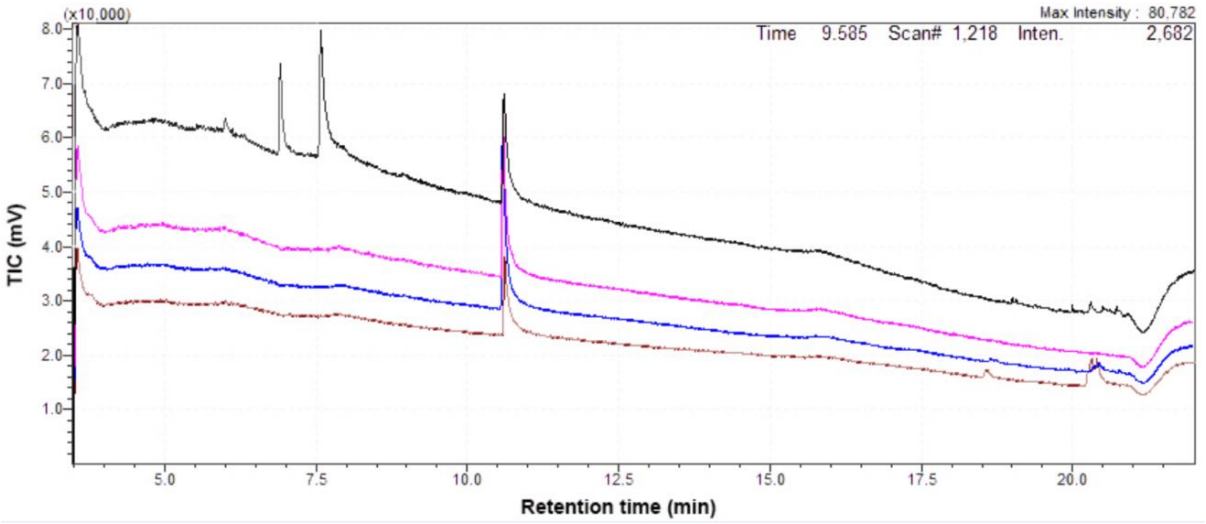

Figure 2: Chromatographic profile GC/MS for the preparation in quadruplicate of MCAS 72 mg/kg and DCAS 66 mg/kg

4.2. Optimization of analytical methods by GC/ECD and GC/MS

Standard solution of MCAS 13 mg/kg and DCAS 12 mg/kg was injected into the GC/ECD, as can be seen in Figure 3 and peaks with intense response were obtained, demonstrating the successful preparation.

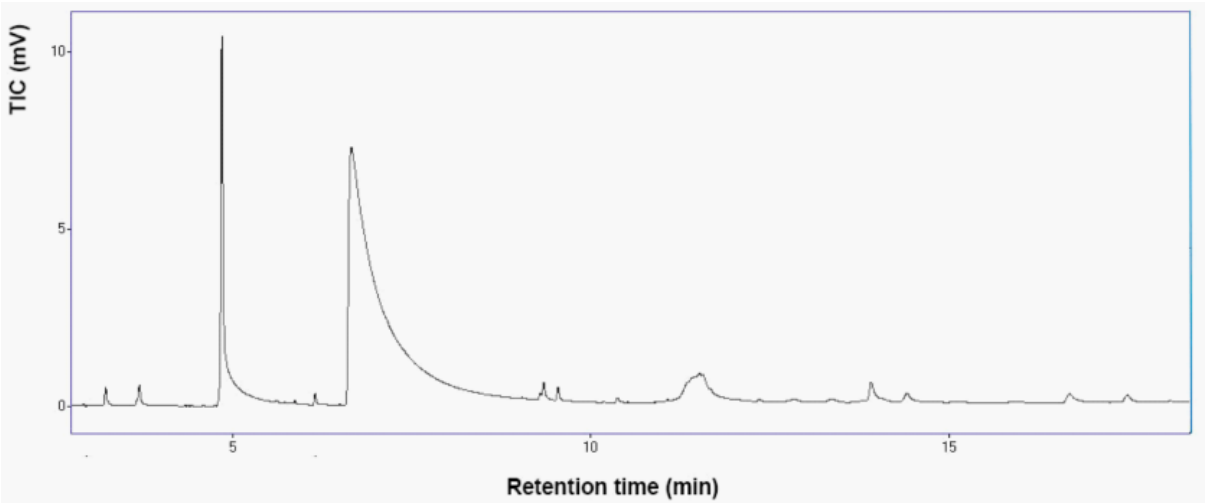

Figure 3: Chromatographic profile in GC/ECD for MCAS 13mg/kg and DCAS 22 mg/kg with retention times 5 e 7 min, respectively

A calibration curve was constructed in order to verify the performance by linearity. Figure 4 shows the calibration curve with a correlation factor > 0.99 for MCAS and DCAS.

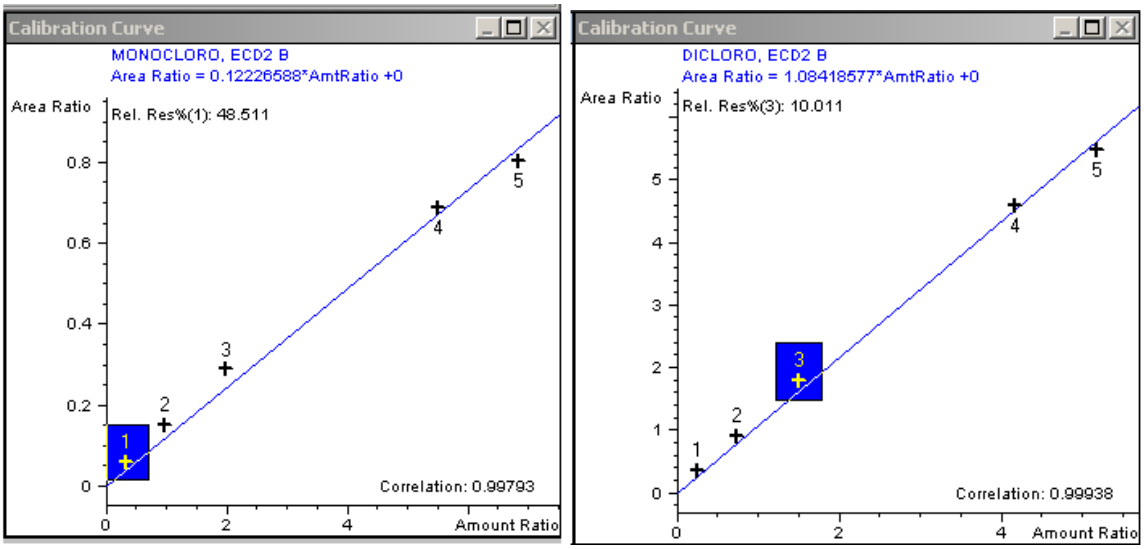

Figure 4: Calibration curves by GC/ECD for MCAS and DCAS

Commercial betaine samples were analyzed with this calibration curve constructed by GC/ECD, the following results were obtained:
• Cocoamido Propyl Betaine, identification 757401, MCAS (14 mg/kg) and DCAS (5 mg/kg)
• Cocoamino Betaine, identification 863451, MCAS (24 mg/kg) and DCAS (9 mg/kg)

The tests in GC/MS Shimadzu QP2010 UP started with reading in "Ion SCAN" in the ratio range m/z 29 to 200. There was no identification of the MCAS and DCAS, indicating the need to change the operation conditions of the gas chromatograph and mass spectrometer to improve the identification (Figure 5).

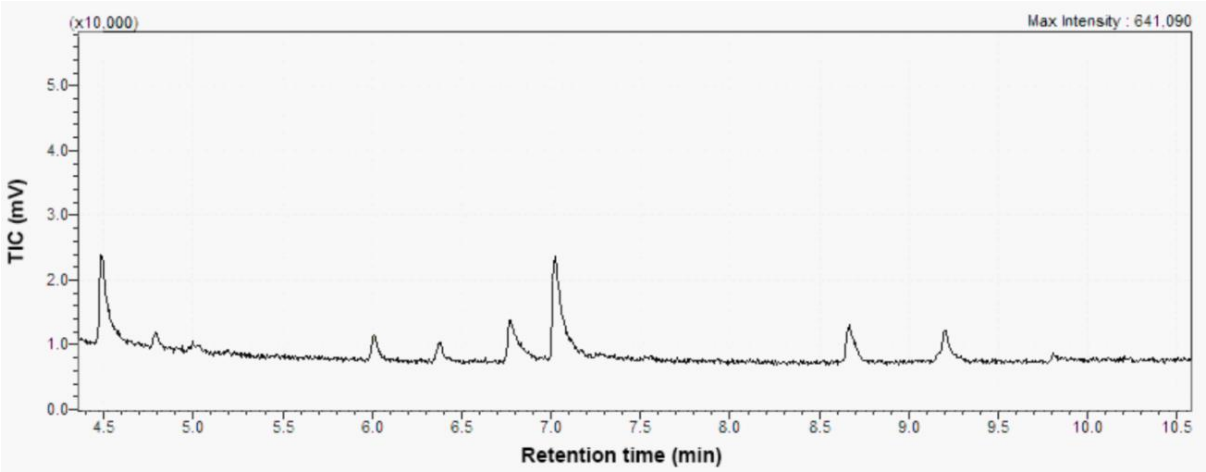

Figure 5: Profile GC/MS in SCAN mode for MCAS to 72 mg/kg and DCAS 66 mg/kg

By GC/MS in SCAN mode was not possible to construct a calibration curve, due to interference of ion-molecule reactions in the mass spectrometer. Analysis by GC/MS mode SIM (Selected Ion Monitoring) was performed [19], and the results were promising: MCAS and DCAS were identified in retention times 5.5 and 7.5 minutes, respectively. Therefore, scan mode SIM was

choose, using the mass/charge ratios of greater intensity – m/z 42, 49, 77, 79 and 94 for the MCAS as shown in Figure 6 and 48, 76, 77, 83 and 85 for the DCAS.

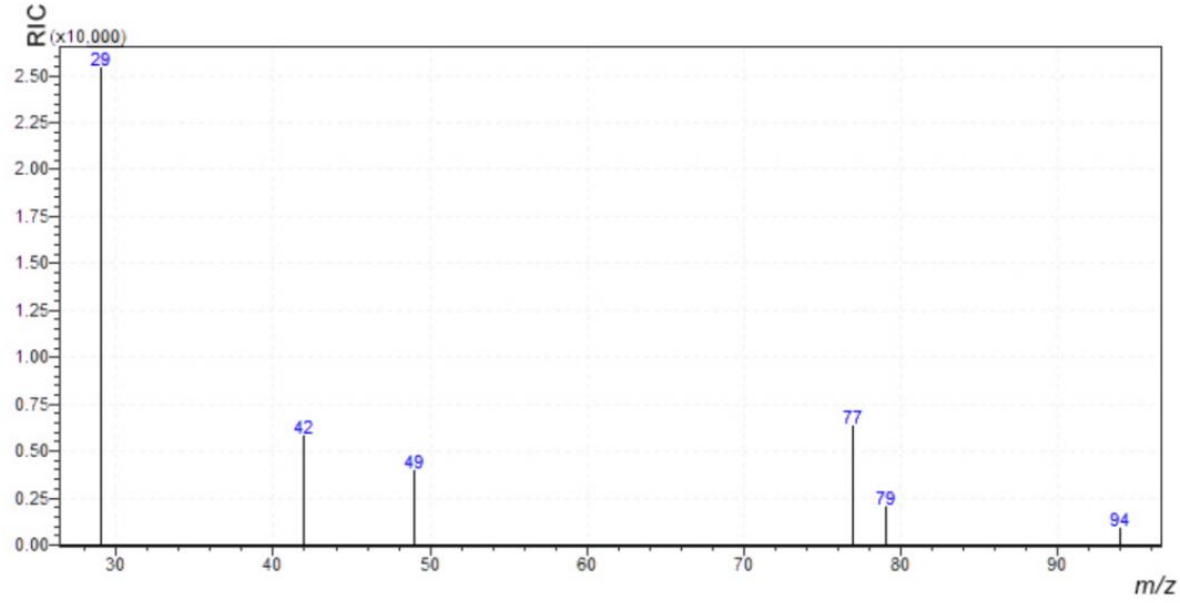

Figure 6: Mass spectrum of the MCAS illustrating intense fragments

Figure 7 presents the chromatogram for MCAS using the GC/MS in SIM mode, which resulted in identification of analyte and response proportional to the concentration.

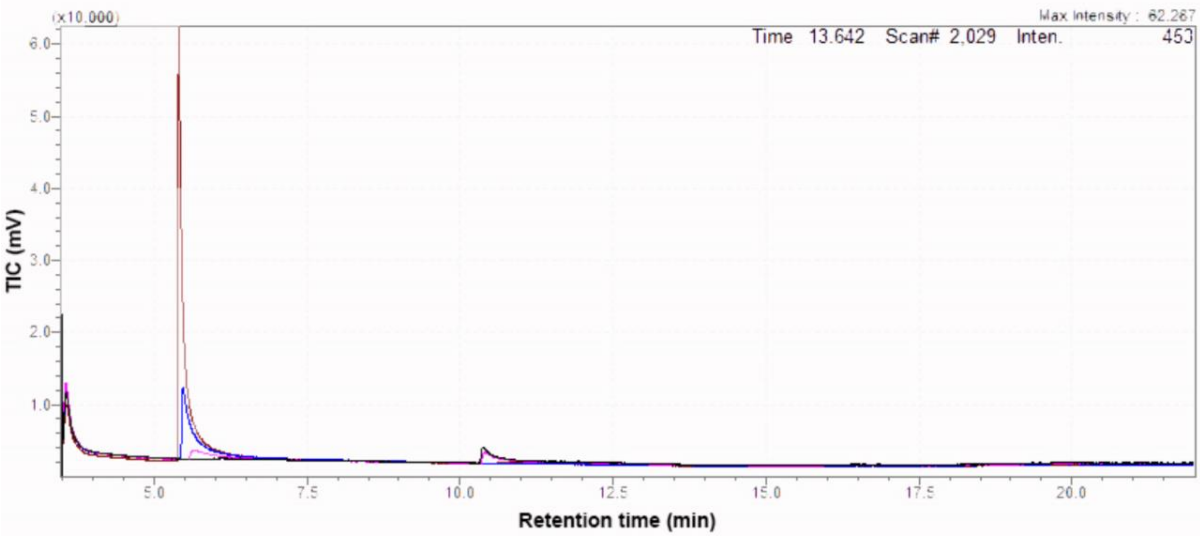

Figure 7: Chromatographic profile GC/MS SIM mode, MCAS 6/18/48/143 mg/kg

The optimization continued by changing the temperature program to drive the peaks in isotherm regions, yielding gain in symmetry. Tests with ratios Split 1:10, 1:20 and 1:40 also were performed and Split 1:10 ratio provides gain in response maintaining the symmetry.

Resolution and symmetry were improved by changing in the heating schedule in the region of interest and the increase in the injector temperature of 250°C to 275°C [20].

When the SIM mode monitors many fragments, upset the analytes identification. The reduction of fragments also causes injury to the answer, since it follows the convenience of working with two or three mass/charge ratios for each analyte.

All optimizations were consolidated in a single method – SIM mode, mass/charge ratios, injector temperature, split ratio and oven temperature schedule - for measuring the gain in resolution, response and symmetry (also in sensitivity by estimate) as illustrated in Figure 8.

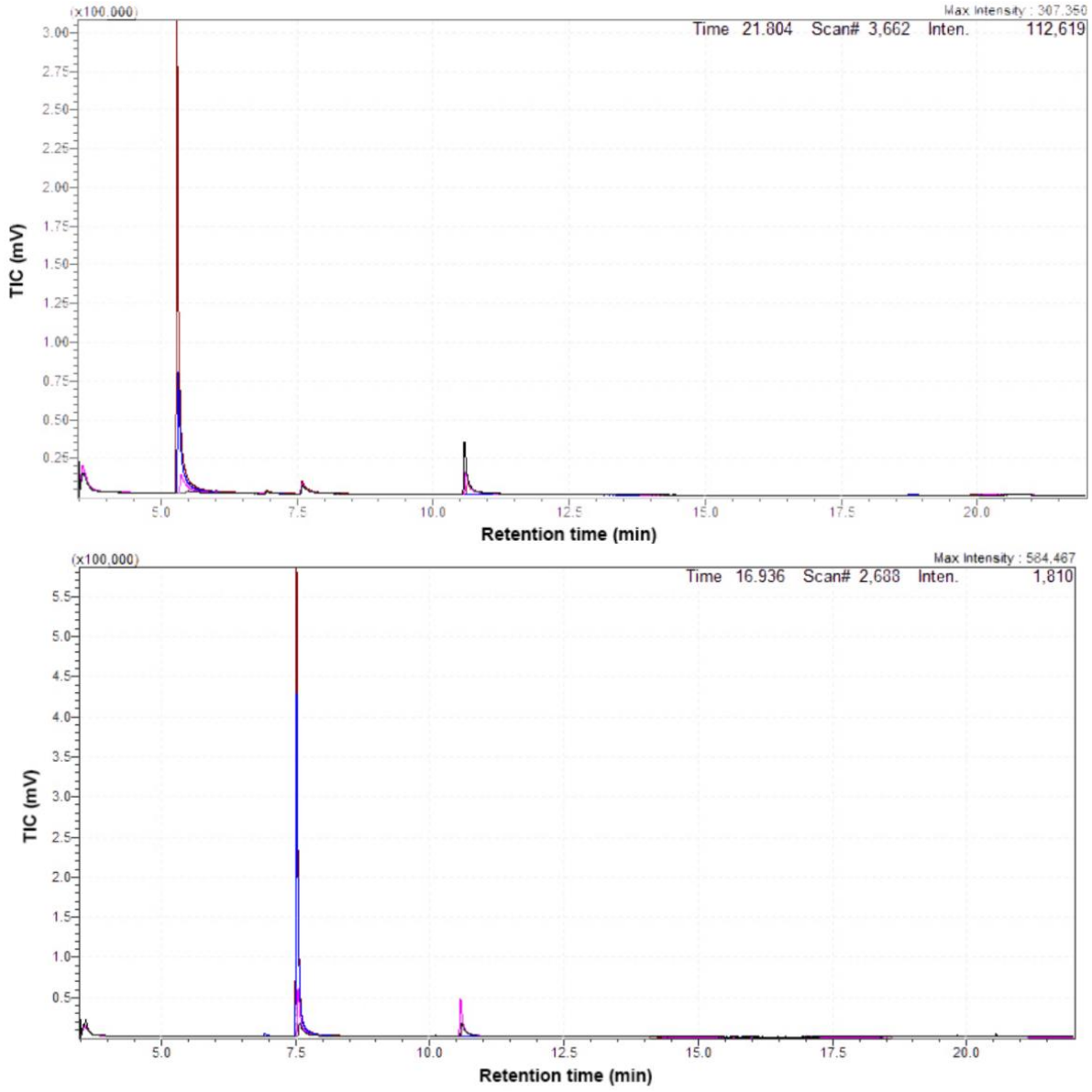

Figure 8: Chromatographic profile in GC/MS SIM mode for MCAS 6/18/48/143 mg/kg (upper) and DCAS 5/15/60/120 mg/kg (lower)

Figure 9 illustrates the calibration curve for MCAS and DCAS in GC/MS. There is a clear opportunity restricting the working range to 5 and 50 mg/kg, improving the linearity.

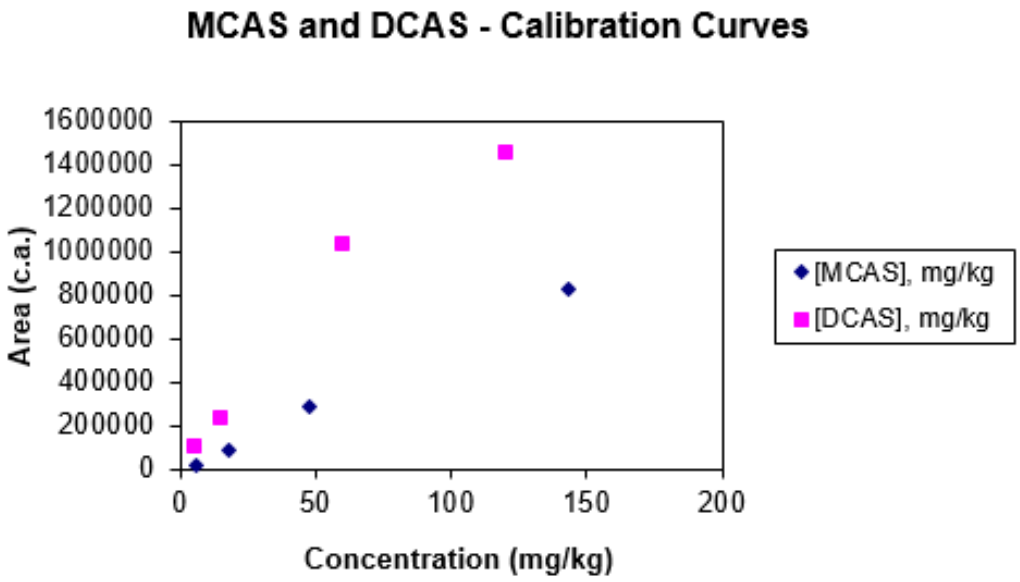

Figure 9: Calibration curves in GC/MS for MCAS and DCAS

Determinations of chloroacetates and their acid forms have alternatives at Ion Chromatography with Conductimetric or UV detection [21] and at High Performance Liquid Chromatography with Photodiode detection [22] or with UV detection [23] and in Capillary Electrophoresis [24]. However, these techniques are not the purpose of this study, which will focus gas chromatography.

For comparison purpose was performed the introduction of solutions of chloroacetic acids 1.5 mg/kg in acetonitrile : water 1: 1 and solutions of ethyl chloroacetates 1.5 mg/kg in acetonitrile: water 1:1 through a capillary in mass spectrometric module AB Sciex Triple Quadrupole in a process known as infusion. The results showed that the typical molecular ions (m/z 94.5, 129, 122.5 and 157) do not present significant intensity and there was a distinct fragmentation than expected according to the NIST database. The LC/MS-MS technique is available in CQMA-IPEN and is relevant to this determination, but no other effort was undertaken by this technique because this is not the purpose of this project.

5. CONCLUSIONS

The sample preparation conditions are relevant regarding the reagents, temperature and time in the esterification and the agitation regime in liquid-liquid extraction.

GC/ECD technique is established with calibration curves, MCAS and DCAS contents of betaine samples were determined into the range 1 and 70 mg/kg.

GC/MS technique has operation conditions defined and calibration curve constructed, and can be optimized in their range of use and sensitivity gain.

This study will allow industries to elect the best technique for their inspections, according to the intended use of the chemical good and the available resources.

ACKNOWLEDGMENTS

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