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ARTICLE

Analytical Method for Residual Monomer Ethyl Acrylate Determination in Commercial Latex Resin using Gas Chromatography with Flame Ionization Detection

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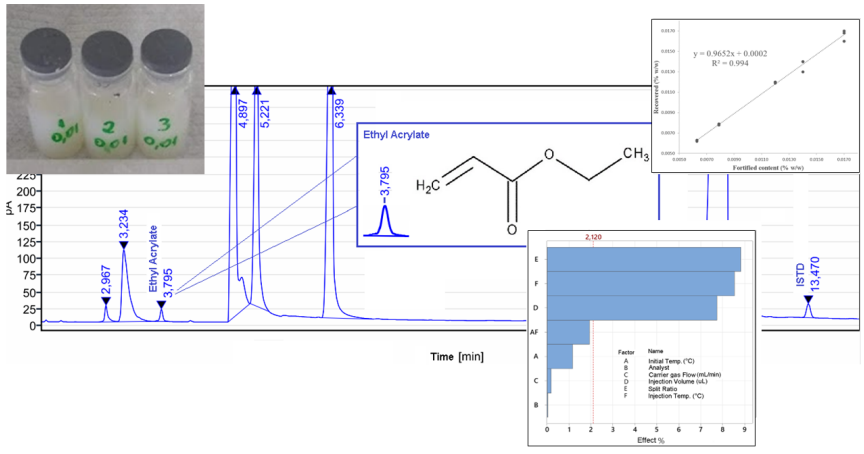

Latex (acrylic resin) produced by emulsion polymerization usually contains variable amounts of residual volatiles (free monomers). Depending on the chemical nature of the monomer, even if these compounds are present in smaller quantities than other volatiles, they can make the latex exude a strong odor and offer toxicity, as with ethyl acrylate, which may make it unfeasible for the consumer to apply the latex. In the present study, a quantitative chromatographic method using gas chromatography with a flame ionization detector (GC-FID) for industrial laboratory determination was investigated. Free ethyl acrylate monomer at a concentration level of 0.010% w/w in a resin-type latex was determined. This method showed selectivity for ethyl acrylate versus other volatiles in the sample, linearity with a coefficient of determination greater than 0.99, limits of detection and quantification of 0.001 and 0.003% w/w, respectively, accuracy and precision with recoveries above 85% and coefficients of variation below 10%. The robustness parameter demonstrated with a Pareto chart shows that the chromatographic parameters of the split ratio, injection volume and temperature impact the method performance.

Keywords: Latex, ethyl acrylate, gas chromatography, method validation

INTRODUCTION

Currently, large paint and varnish industries face the challenge of formulating products that perform well without neglecting the environment and consumer health. Therefore, increasingly sustainable product lines have been manufactured with low concentrations of volatile organic compounds. In this context, acrylic latex represents an important substance that bears significant resemblance to natural latex and

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is extracted from rubber trees. The presence of acrylic binders associated with other polymer ingredients affords several applications, particularly corrosion prevention in coats and paints. Such latexes usually contain variable amounts of residual volatiles such as free monomers. Depending on the chemical nature of the monomer, even if these compounds are present in very small quantities compared to other volatiles, they may cause the latex to exude a strong odor and offer toxicity. Among such volatiles, ethyl acrylate (EA) may cause drowsiness, lethargy, headache, nausea, convulsions, respiratory and gastrointestinal irritation and a long-term carcinogenic effect.[1,2]

Many attempts to detect or quantify ethyl acrylate in latex have involved gas and liquid chromatography techniques. For instance, a hollow fiber protected headspace liquid-phase in conjunction with high-performance liquid chromatography has been introduced to extract and determine three residual monomers: 2-ethylhexyl acrylate, vinyl acetate, and glycidyl methacrylate in polymer latex.[3] Pyrolysis/capillary gas chromatography/mass spectrometry provides information about the chemical nature, polymer monomer composition and sequence distribution of the degraded volatiles. Vu[4] employed this technique to study styrene-ethyl acrylate latexes prepared by different polymerization designs. The use of this technique allows the polymer sequence distribution to be monitored during polymerization.[4] X-ray photoelectron spectroscopy has been applied to analyze the surface chemical composition of cationic fluorinated acrylate copolymer latex films.[5] A more direct form of analysis was used by Petha,[6] who used headspace gas chromatography to determine more than one type of free monomer in resins from emulsion polymerization. The sensitivity obtained for the determination of free monomers using the gas chromatography (GC) method with headspace was 0.4-2.9 mg/kg and 0.9-7.3 mg/kg in terms of the limits of detection and quantification, respectively.[6]

There are some relevant and applicable methods for determining volatile organic compounds in paints, varnishes, resins and related materials, such as the Environmental Protection Agency (EPA) EPA 311 method.[7] However, specifically for the determination of residual monomers that are also considered VOCs in latex resins, such as EA, it is well established and indicated to use GC for determination, following ASTM D 4827-93 and ASTM D 4747-87 test methods.[8,9] Such methods suggest the evaluation of the nature of the latex sample and its variable matrices, type of analytical instrumentation, concentration range of the monomer in the resin, and nature of the monomer itself. The modification of such procedures is recommended, accompanied by the validation of the analytical method.

The goal of the present research was to develop a method for routine analysis using GC-FID without a headspace sampler or other characterization techniques, such as X-ray or mass spectrometry. Therefore, a simple and efficient analytical method to control the residual content of EA monomers in latex resins using GC-FID is proposed here. The analyzed matrix is a water-based product with a low VOC content. Therefore, the concentration range of residual EA in the resin is much lower than that commonly analyzed, since the daily laboratory analysis of the paint industry to control volatiles with a GC-FID addresses analyte concentrations above 0.100% m/m – major volatile compounds or those in solvent-based matrices – whereas AE is determined in a content range 10 times lower and in the water-based matrix.

MATERIALS AND METHODS

Materials

Methyl alcohol (Química Moderna), ethyl acrylate (EA) (99.5%, Dow Chemical) and isobutyl methacrylate (IBM) (99.5%, Dow Chemical) were employed in the sample preparations. Hydrogen (5.0 – White Martins), synthetic air (5.0 – White Martins) and nitrogen (5.0 – White Martins) were employed for GC-FID analysis.

Instrumental Analysis

The gas chromatograph model 7890A was equipped with a flame ionization detector and automatic sampler model G4513A, both of which were produced by Agilent. The following parameters were: temperature of 220-275 °C, a carrier gas flow rate of 4.5-5.5 mL/min, detector gases H_2:N_2:synthetic air at flow rates of 30, 25 and 300 mL/min, sample injection volumes of 1.0-2.0 µL, chromatographic column

Agilent HP-5 (30 m x 0.25 mm x 0.25 m), dilution solvent of methanol and retention time of 3.5-4.0 min for the ethyl acrylate peak.

Preparation of the calibration standard and fortified samples for validation

Ten samples of commercial latex resin were used in this work. The samples were derived from different production batches, and the residual EA monomer content was not detected in the certificate of analysis. After confirming this information with previous analyses, these samples were used as a matrix without the analyte for the fortifications.

To prepare the calibration standard with 1.0% w/w EA and IBM, it was necessary to weigh ca. 50.0 mg of each standard in a 10-mL vial. Methanol was added to 5.0 g; then, each flask was closed and shaken to promote homogenization. Approximately 1.0 mL of this solution was sampled into a 1.5-mL vial for injection into the chromatograph in triplicate as a calibration run to obtain the analyte response factor for subsequent quantification.

To prepare fortified samples for the accuracy and precision tests, a calibration solution of 1.0% w/w was used as a fortification standard. Three concentration levels were prepared (0.005, 0.01 and 0.015% w/w), all in triplicate and on two different days, each day with a different analyst. For each concentration level, 0.0250, 0.0500 and 0.0750 g of the standard was weighed in 10-mL vials. Subsequently, for each preparation, the matrix was added up to a final mass of 5.0 g. Dilution was performed with methanol to approximately 10 mL, followed by homogenization for 10 minutes. Approximately 1.0 mL of each fortified solution was sampled into a 1.5-mL vial for injection into the chromatograph in triplicate.

For the linearity and LD and LQ tests, the same preparation procedure for the accuracy and precision tests was used, adding two more samples of concentrations 0.0075 and 0.0125% w/w, for which 0.0350 and 0.0650 g of the 1.0% w/w standard was respectively weighed. Therefore, 1.0 mL of each solution was sampled in 1.5-mL vials, and triplicate samples of each concentration of 0.005, 0.0075, 0.010, 0.0125 and 0.015% w/w were injected, along with 10 blank samples which were prepared with 5 g of matrix and up to 10 mL of added methanol.

Finally, two samples were prepared for the robustness test, one for each analyst on the same day, with a content of 0.010% m/m following the same preparation and sampling procedure. The injections were designed for 8 experiments, as will be discussed in the results and discussion of this parameter.

Methodology of quantitative analysis and gas chromatography analysis (GC-FID)

The method to determine the EA monomer was quantification with an internal standard (IS). The response factor (RF) of the analyte was first determined with a calibration run of the 1.0% w/w standard in the preparation, which was calculated according to Equation 1. The RF was determined for each day of analysis and in triplicate.

$$RF = \frac{(wa\ x\ AISTD)}{(wISTD\ x\ A)} \qquad \text{Equation 1}$$

where *RF* is the response factor; *wa* is the weight of EA in the calibration standard in grams; *AISTD* is the % area produced by the peak of the IS IMB; *wISTD* is the mass of the MIB ISTD in the calibration standard in grams; and *A* is the % area produced by the EA peak.

With the calculated RF, the determination of EA in the fortified samples for each evaluated parameter was performed according to Equation 2.

$$C\ (\%)\ = \frac{(wpi\ x\ RF\ x\ A\ x\ 100)}{(ws\ x\ AISTD)} \qquad \text{Equation 2}$$

where *C* (%) is the EA concentration in % w/w; *RF* is the response factor; *ws* is the sample weight; *AISTD* is the % area produced by the peak of the IS IBM in the chromatographic run of the sample; *wpi* is the weight of the IS MIB added to the sample; and *A* is the % area produced by the EA peak in the chromatographic run of the sample.

Validation parameters and acceptance criteria

The performance parameters that can be addressed in quantitative method validation studies are the selectivity/specificity, linearity, detection and quantification limits, accuracy, precision (repeatability and intermediate precision) and robustness. The parameters in the present work are:

Selectivity/Specificity

For selectivity and specificity, the chromatogram of a blank matrix was compared to that of a matrix fortified at 0.005% w/w.

Accuracy and Precision

Accuracy was evaluated through the percent recovery (Rec %) (Equation 3) of the analyte in fortified samples at three concentration levels in relation to the target content: 50%, 100% and 150%. For each concentration level, three fortified samples were prepared, and three readings were taken to yield a total of nine assays per concentration level. Two days of accuracy testing were performed with different analysts each day. Precision was evaluated using the coefficient of variation (CV %) (Equation 4) at the repeatability and intermediate precision levels.

$$Rec\ \% = \frac{C1}{C2} \times 100 \qquad \text{Equation 3}$$

where *C1* is the concentration obtained in the test, and *C2* is the fortified concentration

$$CV\ \% = \frac{standard\ desviation}{average} \times 100 \qquad \text{Equation 4}$$

Linearity, Limits of Detection (LOD) and Quantitation (LOQ)

Linearity was evaluated based on a study of recoveries obtained with samples fortified at five concentration levels (0.005; 0.0075; 0.010; 0.0125 and 0.015%), all of which were injected in triplicate. The LOD and LOQ were determined using Equation 5,[9] which approaches the average of 10 baseline noise measurements of blank samples at the EA retention time.

$$LOD(LOQ) = \frac{k\ .\ r}{a} \qquad \text{Equation 5}$$

where *k* is the constant for the limit of detection (*k* = 3) and quantification (*k* = 10); *r* is the average of 10 measurements; Area % pertains to noise of blank injections; and a is the slope of the linear regression between Area % versus recovered grade (% w/w).

Robustness

The robustness parameter was evaluated following the Placket-Burmann experimentation matrix. For this test, eight experiments were performed with a factorial combination of 6 factors at two levels, with each experiment performed in triplicate. The parameters and levels are shown in Table I.

Table I. Placket-Burmann experiment matrix for the robustness test

	Experiments							
Parameters	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Initial temperature (°C)	45	45	45	45	40	40	40	40
Analyst	B	B	A	A	B	B	A	A
Carrier gas flow (mL/min)	5.0	4.8	5.0	4.8	5.0	4.8	5.0	4.8
Injection Volume (µL)	1	1	2	2	2	2	1	1
Split ratio	01:10	01:25	01:10	01:25	01:25	01:10	01:25	01:10
Injection temperature (°C)	175	170	170	175	175	170	170	175

RESULTS AND DISCUSSION

Exploratory Analysis

To find the best analysis conditions in the GC-FID, a study was performed with respect to the ranges of the analytical parameters described in the chromatograph usage parameters.

The best oven temperature condition was programmed with an initial temperature of 40 °C for 4 minutes, an increase in temperature with a first heating ramp at a rate of 4 °C/min to 68 °C and a second ramp at a rate of 3 °C/min to 92 °C, which best separated the volatiles in the mixture. In conjunction with this programming, a carrier gas flow rate of 4.8 mL/min, a split ratio of 1:25, and injector and detector temperatures of 250 °C and 275 °C, respectively, were used. For this first evaluation, 2 µL of a 1.00% w/w standard mixture of all volatiles in the product formulation was injected. A positive result was obtained with this test because total separation of all components of the mixture was observed, as shown in Figure 1.

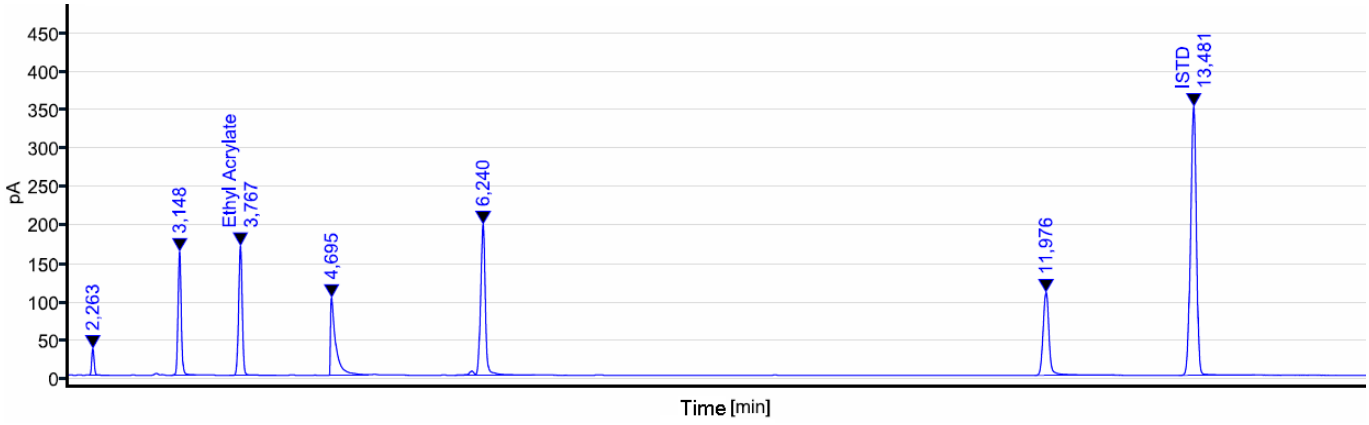

Figure 1. Chromatogram generated by injecting a prepared standard containing all volatile components in the sample formulation for the chromatographic separation evaluation.

Exploratory experiments were performed to identify the best conditions for the chromatographic assay of latex samples. For this purpose, samples of the latex resin fortified at a concentration level close to the target level of 0.01% w/w were used, and 3 experiments were performed with injections by varying the injector and detector temperature and split ratio and maintaining the other parameters. Experiment 1 was performed using a split ratio of 1:25 and injector and detector temperatures of 250 °C and 275 °C, respectively. Experiment 2 was performed using a split ratio of 1:25 and injector and detector temperatures of 170 °C and 220 °C, respectively. Finally, Experiment 3 was performed with conditions identical to those of Experiment 2, only with the split ratio changed to 1:10.

These parameters were chosen for optimization because a deviation from the baseline near the peak of interest in the chromatographic run of the fortified sample was observed using the initial chromatographic method (Experiment 1), as shown in Figure 2 (a). This effect may be related to the high temperatures of the injector and detector initially used with the standard mixture, which can be justified by some degradation or reaction of the analyte with the matrix due to the higher temperature. The chromatogram of Experiment 2 of the exploratory analysis is shown in Figure 2 (b), where lower injector and detector temperatures and a similar split ratio to the initial ratio were employed. In addition, the split ratio was varied, since the concentration that one aims to quantify is low for the standards of this type of analysis, as previously mentioned. Thus, a lower ratio was chosen compared to the initial method to identify a possible increase in analyte signal. The chromatogram for Experiment 3 is shown in Figure 2 (c).

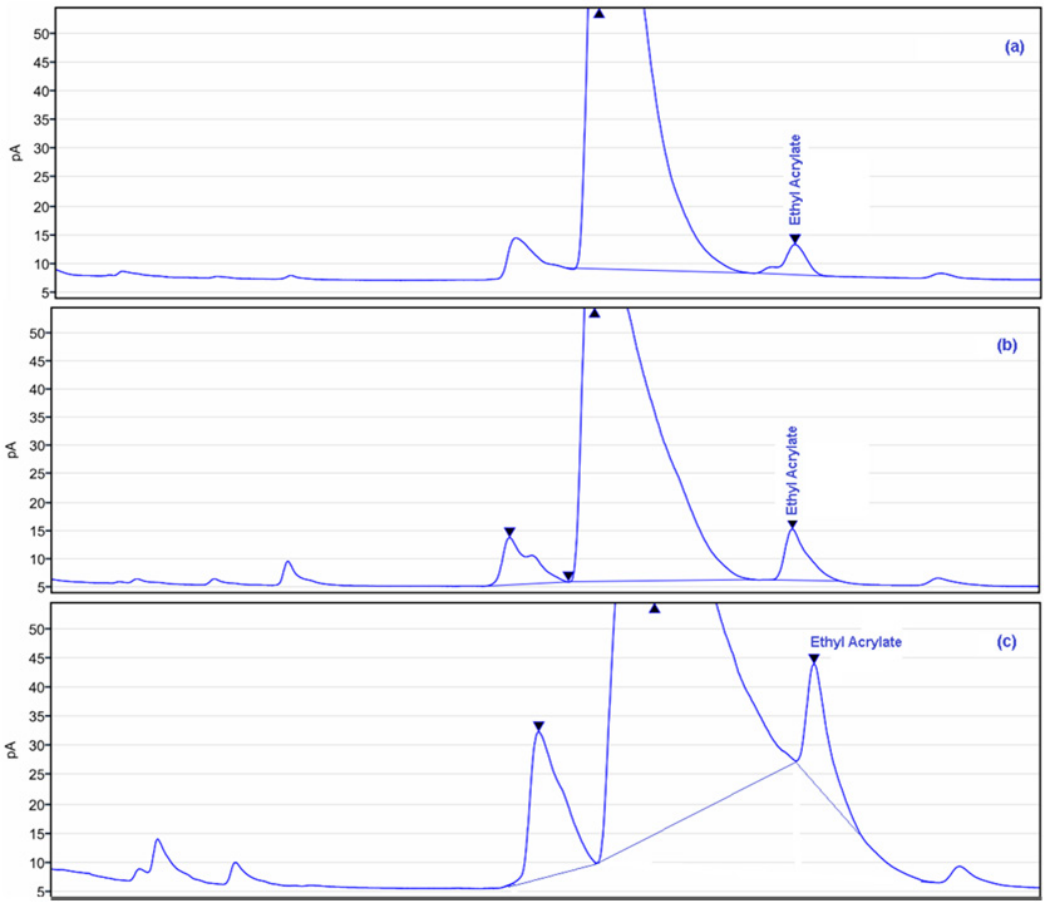

Figure 2. (a), (b) and (c) Chromatograms of the assay of the fortified sample of Experiments 1, 2 and 3, respectively. Experiment 1 was performed using a split ratio of 1:25 and injector and detector temperatures of 250 °C and 275 °C. Experiment 2 was performed using a split ratio of 1:25 and injector and detector temperatures of 170 °C and 220 °C. Experiment 3 was performed with the same conditions as Experiment 2, only changing the split ratio to 1:10.

Some observations can be made based on the results of the three experiments:

(a) By maintaining the temperature programming of the initial methodology, total separation of the volatile components in the mixture was obtained.

b) Using lower temperatures in the injector and detector than initially proposed, it was possible to eliminate the problem of deviation of the baseline near the peak of the analyte.

c) The split ratio of the initial method was maintained, since with a ratio of 1:10, a very pronounced coelution effect between the analyte of interest and another component in the matrix was observed.

When the best conditions of analysis were reached, relevant tests were initiated for each validation parameter: Selectivity/Specificity; Accuracy and Precision; Linearity, LD and LQ and Robustness.

Selectivity/Specificity

The selectivity and specificity of the method can be demonstrated by comparing the chromatograms of injections of the blank, a matrix without analyte, and a sample fortified at a level of 0.005% w/w, as shown in Figures 3 (a) and (b).

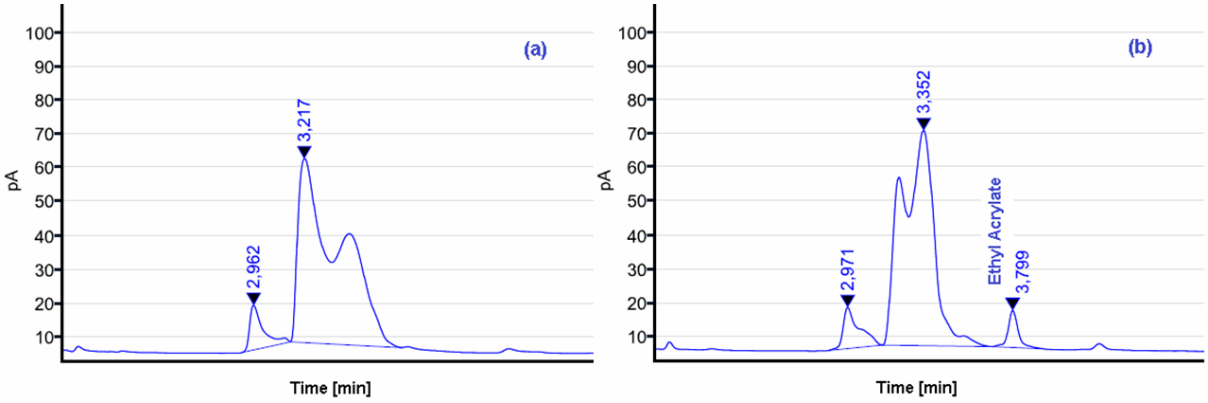

Figure 3. Chromatographs of (a) blank and (b) sample fortified with 0.005% w/w EA.

A comparative analysis between the chromatograms of the blank and the fortified sample shows that no characteristic chromatographic peak of the analyte was observed in the blank sample, but in the fortified sample, it is possible to identify the peak of the analyte separately from other volatiles that compose the matrix, and this parameter was within the acceptance criteria.

Accuracy and Precision

Accuracy was evaluated by the percent recovery (Rec %) of the analyte in fortified samples at three concentration levels relative to the target content: 50%, 100% and 150%. For each concentration level, three fortified samples were prepared, and three readings were taken for each sample, yielding a total of nine assays per concentration level. Two days of accuracy testing were performed with different analysts each day. The precision was evaluated using the coefficient of variation (CV %) at the repeatability and intermediate precision levels. For repeatability, the results of the two days of accuracy testing were individually used to evaluate the CV % of the triplicates for each of the three samples of each level on each day and the CV % obtained at each level. For intermediate precision, the two days of accuracy testing were taken together, and the values of CV % of the recoveries between the two days were evaluated. In addition, Student's t test was performed between the recoveries at each concentration level with 95% confidence to verify that the results of the recoveries for the two days were statistically equal to 100%. The results for accuracy, repeatability and intermediate precision are shown in Tables II and III.

Table II. Accuracy

Analyte concentration	Day 1 - Analyst 1				Day 2 - Analyst 2			
	Average (%)	CV (%)[a]	Average level (%)	CV level (%)[b]	Average (%)	CV (%)[a]	Average level (%)	CV level (%)[b]
Level 1 0.005%	96.9	0.16	96.1	2.71	90.3	3.6	95.3	4.59
	98.1	1.58			97.5	2.59		
	93.1	4.16			98.2	1.09		
Level 2 0.010%	93.1	2.79	90.5	4.21	91.5	6.76	92.6	4.28
	92.4	7.07			89.3	6.93		
	86.2	8.98			97	1.93		
Level 3 0.015%	87.8	6.05	89.1	1.46	97.4	1.2	96.5	3.36
	89.1	4.72			99.1	0.83		
	90.4	5.08				7.67		

[a] The values of CV (%) in the third and seventh columns refer to the triplicate samples analyzed for the 3 experiments performed at each level.

[b] The CV level (%) values present in the fifth and ninth columns refer to the variation within the test level: that is, considering the average level obtained.

Table III. Intermediate precision

Analyte concentration	Average Rec (%)	SD (%)	CV (%)	Student *t* Test
Level 1 0.005%	95.7	0.538	0.562	-11.3
Level 2 0.010%	91.6	1.452	1.586	-8.18
Level 3 0.015%	92.8	5.181	5.584	-1.96

To determine Rec % and CV %, Equations 3 and 4 were used. To conduct Student's *t* test$_{(0.05;1)}$, the Equation 6 was used:

$$t = \frac{Average\ Rec\ (\%) - 100\ \%}{SD/\sqrt{n}} \qquad \text{Equation 6}$$

where *Average Rec* (%) is the average percentage recovery per level between days; *SD* is the standard deviation of recovery levels between days; and n is the number of repetitions.

Based on the results of accuracy, repeatability and intermediate precision, all of these parameters were within the previously established acceptance criteria, Rec % was 85-100%, and CV % was smaller than 10%. Furthermore, the average of the Rec % results between test days and for each concentration level of both days, except for level 3 on Day 1, were within the range proposed by INMETRO[10] to evaluate the

accuracy through recovery assay, which suggests a recovery range of 90-107% for the target concentration. In the CV % results, the CV % values of the concentration levels of the two-day test are within the proposed range of INMETRO,[10] which suggests a CV % of up to 5.3% to assess the repeatability in this concentration range. Although the result between days for a concentration of 150% of the target content exceeded 5.3%, this result is within the acceptance criteria established for this work. Finally, Student's *t* test was performed with a 95% confidence level to verify the accuracy of the intermediate precision measurements. For this configuration, there is a critical *t* of 12.71, as shown in Table III; all test results had smaller values than the critical *t*, which indicates that the recovery values can be considered 100%.

Linearity, LOD and LOQ

The linearity was evaluated from a study of recoveries obtained with samples fortified at five concentration levels (0.005; 0.0075; 0.010; 0.0125 and 0.015%), which were all injected in triplicate. With this approach and the evaluation of the coefficient of determination (R^2) of a linear regression between fortified and recovered levels, as shown in Figure 4, it is possible to affirm whether the method exhibits sufficient linearity.[11] The quantitative method employed for chromatographic analyses in this study was internal standardization.[8,11]

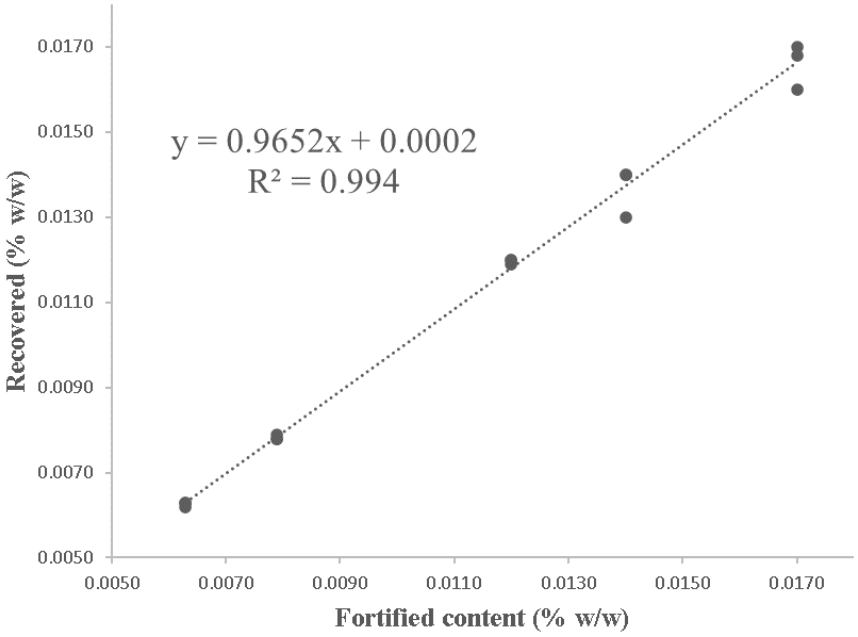

Figure 4. Linear regression between recovered content (% m/m) and fortified content (% w/w) for the linearity evaluation.

The R^2 value obtained in the linear regression was 0.994, which is not consistent with the referred minimum for this type of linearity analysis methodology,[11] which is an R^2 of at least 0.995. However, the relative percentage error obtained between these two values was only 0.1%, and the value found for R^2 was within the acceptance criteria stipulated for this work, which was at least 0.99. Therefore, a result between the acceptance criterion and the one referred to for this methodology was obtained. Furthermore, it can be stated that, as in Petha,[6] a satisfactory result for the linearity assay was obtained, with an R^2 of 0.99, although the method and approach for the linearity assay were done differently: Petha[6] utilized a calibration curve with a concentration range, and the current study used the comparison between recovered and fortified content.[11]

The LOD and LOQ were determined using Equation 5, which addresses the average of 10 baseline noise measurements of white samples at the retention time of the AE and the angular coefficient of the linear regression between the chromatographic peak area results of the AE and the respective levels determined by internal standardization.[11] The graph of the performed regression is shown in Figure 5.

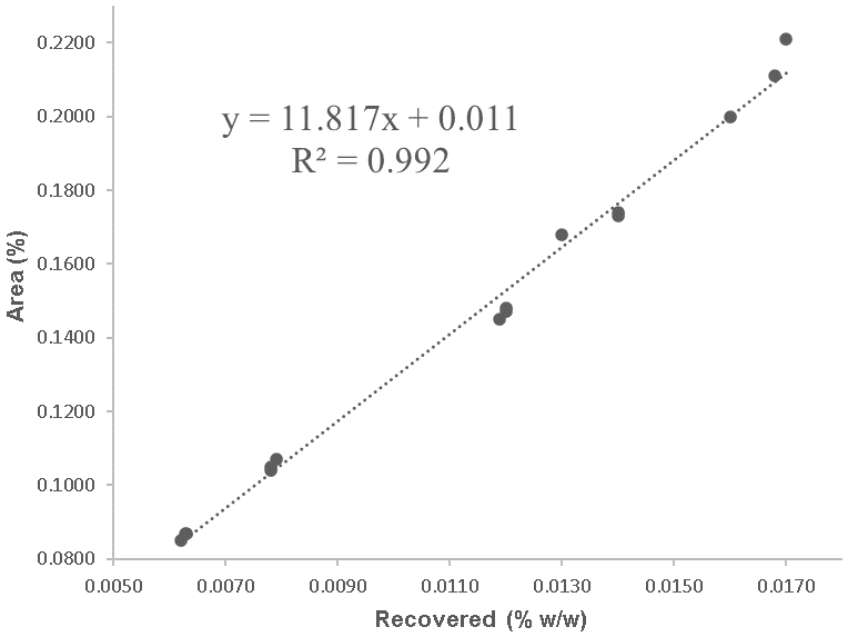

Figure 5. Linear regression between AE peak area (%) and recovered content (% w/w) determined by internal standardization for the LOD and LOQ evaluation.

The LOD and LOQ results were 0.001 and 0.003% w/w, respectively, and the relevant regression R^2 was 0.992. Thus, R^2 satisfied the acceptance criterion. Furthermore, the LOD and LOQ are below the target content in this work (0.010% w/w), and contents above the LOD and LOQ can be detected and quantified with accuracy and precision,[10] as confirmed by the accuracy and precision values, where concentrations of 0.005, 0.010 and 0.015% were used. It is worth noting that even for a method in which clean-up methods or a headspace sampler were not used, in addition to not using a detector with higher sensitivity, such as the mass spectrometer, the LOD and LOQ values of 10 and 30 ppm found are remarkable. Petha[6] found average LOD and LOQ values of 1.5 and 5.0 ppm, respectively; however, in his study, a high-performance headspace sampler and mass spectrometer were utilized, while the current study used only a GC-FID and a simple sample preparation method.

Finally, the linearity study was analyzed to further confirm the accuracy of the method and examine the effect of the matrix for the EA determination, since all assays were performed by adding the EA standard in a matrix free of analyte. The angular and linear coefficients of the regression between recovered and fortified contents were evaluated (Figure 6), and Student's *t* test was performed (Equations 7 and 8).[9]

$$ta = \frac{1 - a}{Sa} \qquad \text{Equation 7}$$

$$tb = \frac{b}{Sb} \qquad \text{Equation 8}$$

where ta is the calculated t for the angular coefficient; a is the angular coefficient of the linear regression; Sa is the estimated standard deviation of the angular coefficient; tb is the calculated t for the linear coefficient; b is the linear coefficient of the linear regression; and Sb is the estimated standard deviation of the linear coefficient.

To obtain the results for Sa and Sb and the other linear regression parameters, a regression test was performed with the Microsoft Excel® software data analysis add-in. Sa and Sb were 0.02120 and 0.00026, respectively. As a result, ta and tb were 1.64 and 0.87, respectively. The tabulated critical t for this test was 3.01; i.e., both calculated t values were below criticality, which indicates that statistically, a = 1 and b = 0.[11] Therefore, two affirmations can be made with these results: there is consistency between recoveries and fortifications, and the matrix effect to determine this analyte is not significant.

Robustness

The robustness parameter was evaluated following the Placket-Burmann experimentation matrix.[10] For this test, 8 experiments with factorial combination of 6 factors at two levels were performed, and each experiment was performed in triplicate. The results are shown in Table IV.

Table IV. Placket-Burmann Matrix Results

Results	Experiments							
	1	2	3	4	5	6	7	8
Fortified (% m/m)	0.0103	0.0103	0.0110	0.0110	0.0103	0.0103	0.0110	0.0110
Rec (%) 1	86.4	94.2	69.1	89.1	98.1	63.1	88.2	96.4
Rec (%) 2	96.1	99.0	67.3	98.2	100.0	59.2	87.3	90.0
Rec (%) 3	98.1	99.0	61.8	98.2	93.2	57.3	100.0	97.3
Average Rec (%)	93.5	97.4	66.1	95.2	97.1	59.9	91.8	94.5
SD Rec (%)	6.24	2.80	3.78	5.25	3.50	2.97	7.10	3.96
CV (%)	6.67	2.88	5.73	5.52	3.61	4.95	7.73	4.19

The effects of the variables on method performance are shown in the Pareto chart (Figure 6), which was obtained using Minitab 2019® software.

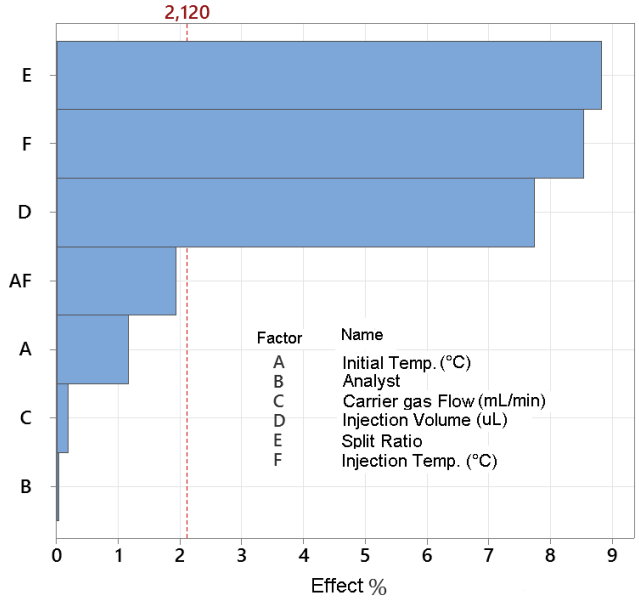

Figure 6. Pareto chart: relationship between the parameters and the % effects of the variations of each parameter on the recovery of the analyte.

From the Pareto diagram, the three parameters evaluated in the robustness test resulted in percentage effects above the critical effect of 2.120 and affected the analyte recovery result. According to the diagram's notation: E) split ratio; F) injector temperature and D) injection volume.

In the exploratory analysis, impacts on the chromatographic analysis were detected when the split ratio and injector temperature factors were varied. As discussed, the injector temperature influenced the shape of the analyte peak, so this parameter positively contributes to the analysis when the temperature is lower (170 °C). For the split ratio parameter, with a lower ratio of 1:10, the coelution effect of the analyte with another component occurs, which decreases the peak area, and the recovered analyte content affects the recovery result, as demonstrated by its effect above the critical effect. There is also the effect for the injection volume parameter, which may be linked to the split ratio, because when a larger sample volume is injected while maintaining a low split ratio, a larger amount of sample is inserted into the chromatographic column, which can enhance the coelution effect in the exploratory analysis and justify its effect above the critical level in the Pareto chart.

Finally, only the results of Experiments 3 and 6 were not within the acceptance criteria for recovery (between 85 and 100%), which can be justified by the previous discussion of the split ratio and injection volume parameters, since the injection volume was 2 µL and the split ratio was 1:10 in these two experiments. When CV % was evaluated, all experiments were within the acceptance criteria (up to 10%), which indicates acceptable precision in the results.

CONCLUSIONS

The results show that the methodology reached the previously established acceptance criteria. It showed selectivity for ethyl acrylate versus other volatiles in the sample, linearity with a coefficient of determination greater than 0.99, limits of detection and quantification of 0.001 and 0.003% w/w, respectively, accuracy and precision with recoveries above 85% and coefficients of variation below 10%. The robustness parameter in the Pareto chart shows that the chromatographic parameters of split ratio, injection volume and temperature impact the method performance. The study proves the viability of determination with simple instrumentation and low cost using GC-FID equipment.

Conflicts of interest

The authors declare no conflicts of interest.

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