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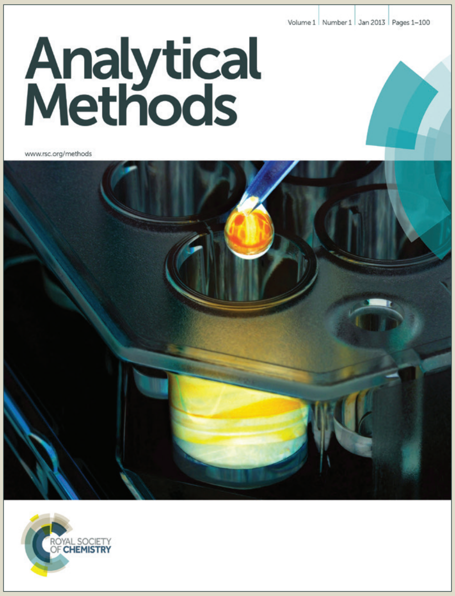

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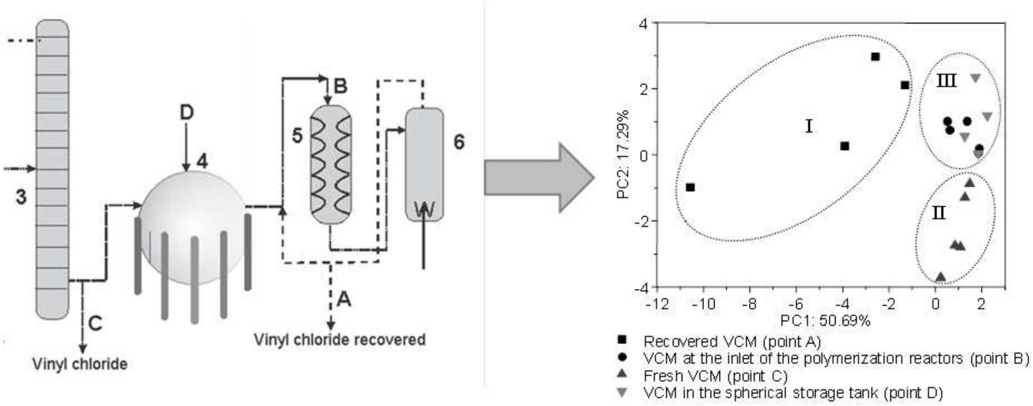
VCM was analyzed for impurities, using TDA-GC-MS and PCA multivariate analysis; nineteen substances were identified; significant differences were found in the VCM, depending on the point in the process where samples were collected.



Development of a Method for the Identification of Organic Contaminants in Vinyl Chloride Monomer (VCM) by TD-GC-MS and Multivariate Analysis

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Abstract

The main raw material used in the production of polyvinyl chloride (PVC) is vinyl chloride monomer (VCM). Controlling the purity of VCM is essential to control the parameters of the polymerization reaction and the properties of PVC resins, such as molecular weight, porosity, particle size and thermal stability, since some organic contaminants react as co-monomers and are undesirable. Two methods of concentration by adsorption and thermal desorption were developed using the adsorbents Tenax-TA and Tenax-TA/Carboxen1000/CarbosieveSIII, applying full and fractional factorial design to optimize the variables. Organic contaminants were identified in the various stages of production, storage and recovery at four distinct points in the process, leading to the identification of nineteen substances in all the samples, including aliphatic and aromatic hydrocarbons, organochlorines, alcohols, phenols and phenones. The contaminants that showed the highest relative abundances were styrene, benzene, toluene, naphthalene, 1,2-dichloroethane, 1-octanol and 1,3-butadiene. Among these contaminants, 1,3-butadiene and styrene have been reported in the literature as potent inhibitors of VCM polymerization. Using PCA multivariate analysis, it was possible to confirm that there are statistically significant differences in the characteristics of the VCM. Samples from four different points in the process were successfully classified into three different groups, in each of which the main contaminants responsible for the differentiation of the samples were identified. This work is innovative in the application of a TD-GC-MS-based system, for the identification of organic contaminants in VCM produced industrially, and in the investigation of its process by multivariate analysis.

Keywords: Vinyl chloride monomer, contaminants, TD-GC-MS, Principal Component Analysis

Introduction

Polyvinyl chloride (PVC) is a highly versatile thermoplastic resin that has been used in the manufacture of products used in the fields of medicine, food, construction, automotive, toys, etc.[1,2] The main industrial process for obtaining PVC, which corresponds to about 80% of commercial processes, is polymerization of vinyl chloride monomer (VCM) in an aqueous suspension.[3,4]

VCM is produced from 1,2-dichloroethane (DCE) in commercial manufacturing processes. DCE can be produced from the reaction between ethylene and chlorine or from anhydrous hydrogen chloride (HCl) with ethylene, in the presence of oxygen. Lastly, DCE is converted by pyrolysis into VCM and anhydrous hydrogen chloride (HCl).[5,6]

Contaminants in VCM originate from the raw materials and chemical reactions involved its production process.[5,7] Ethylene, which is the main raw material of direct chlorination and of oxychlorination, is obtained by catalytic cracking processes, during which dehydrogenation and breaking reactions occur with the saturated petroleum and naphtha hydrocarbons molecules.[5] Due to the nature of this process, ethylene may contain impurities such as saturated, unsaturated and aromatic hydrocarbons. Chlorinated derivatives of these hydrocarbons and ethylene are contaminants reported to be byproducts of oxychlorination.[7,8] In the formation reaction, various byproducts may be formed in addition to 1,2-dichloroethane (DCE), such as 1,1,2-trichloroethane, trichloroacetaldehyde, *cis* and *trans* 1,2-dichloroethene, chloromethane, dichloromethane, and tri- and tetrachloromethane.[7,8] On the other hand, the main byproduct of direct chlorination is 1,1,2-trichloroethane, while acetylene, 1,3-butadiene, 2,4-hexadiene, chloromethane, chloroethane, 2-chloro-1,3-butadiene, 2-chloropropene-1, benzene, acetaldehyde, trichloroethylene, trichloromethane and tetrachloromethane can be formed in the pyrolysis of DCE to form vinyl chloride.[7-9] These contaminants may be present in the monomer that will be used in the production of PVC, even after successive purification steps, and are potential interferents in radical polymerization, through secondary reactions that form structures, with chlorine atoms bound to allylic and tertiary carbon or oxygenated groups.[9,11] In polymerization, VCM contaminants can increase the reaction time and diminish the conversion of VCM into PVC.[10] Alterations in the properties of PVC, such as uncontrolled particle size, color changes, and reduced thermal stability, porosity, apparent density and average molecular weight, have also been reported.[9,10] While the effects of some organic contaminants of VCM are already known and reported in the literature, others require studies to elucidate their effects on the polymerization and properties of the PVC.[9,12] Thus, it is crucial to control the purity of VCM in order to control the polymerization reaction and properties of PVC, which in turn requires identification of the compounds that are present as contaminants of the monomer in the various stages of its production, storage and recovery.

Since most of the contaminants of VCM are volatile and semi-volatile organic compounds, that are present at low concentrations, in a matrix whose physical and chemical properties closely resembles those of these compounds, the use of an adsorption preconcentration method allows for their selective retention and preconcentration. The analysis of samples and identification of the compounds can be performed using a thermal desorption (TD) system coupled to a gas chromatography-mass spectrometry (GC-MS) system.[13,16] On the other hand, the Principal Component Analysis (PCA) is an exploratory statistical procedure that uses correlated variables, to enable the visualization of clusters of samples and the variables responsible for them.[17,18]

In this work, a method based on TD-GC-MS was developed for the identification and determination of the concentration profiles of organic contaminants in vinyl chloride monomer (VCM) produced in an industrial process. Principal Component Analysis was applied for the discrimination of VCM collected in different stages of the production, storage and recovery process.

Experimental Section

Sampling

The VCM samples were collected and its contaminants preconcentrated on-site at an industrial plant producing VCM and PVC, located in the Industrial Pole of Camaçari, Bahia, Brazil. The samples were collected in stainless steel cylinders (equipped with Hoke PV 62y valves, 6000 PsiG, 12.0 Kgf cm^{-2} working pressure and 300 mL capacity) after recirculation of the VCM stream, at four points of the plant: at the exit from the VCM distillation tower (freshly produced VCM); from the spherical storage tanks; at the entry of the polymerization reactors, and after the recovered VCM distillation tower.

Optimization of the adsorption conditions

The samples' preconcentration conditions were optimized for two types of adsorbents differing from each other in chemical structure, surface area, pore structure and thermal stability, which resulted in complementary retention capacities for the different types of compounds found in the samples. The conditions of flow rate and sample volume were optimized using a full factorial design (2^2) for which the response variable was the sum of the areas of the chromatographic peaks, with three replications at the central point, resulting in seven experiments, as described in Table 1.

Table 1 – Levels of the factors of the 2^2 factorial design

Factors	-1	0	+1
Flow (mL min^{-1})	20	30	40
Volume (L)	1.0	1.5	2.0

Optimization of the thermal desorption conditions

Initially, an investigation was made of the effects of six variables on the thermal desorption of the retained compounds, using a $2^{(6-2)}$ fractional factorial design with three replications at the central point, making a total of nineteen experiments, as described in Table 2. The six factors under study were temperature (Td1), time (td1) and flow (Fd1) of the first thermal desorption (from the sample adsorbent to the focusing trap), time (td2) and temperature (Td2) of the second thermal desorption (from the focusing trap to the GC column) and the type of adsorbent of the focusing trap (Aft).

Table 2 – Levels of the factors of the $2^{(6-2)}$ fractional factorial design for the thermal desorption of the adsorbents Tenax-TA and Tenax-TA/Carboxen1000/CarbosieveSIII

Factors	-1	0	+1
Temperature of the 1st desorption (Td1) (°C)	250	275	300
Time of the 1st desorption (td1) (min)	20	25	30
Desorption flow (Fd1) (mL min^{-1})	20	40	60
Temperature of the 2nd desorption (Td2)	250	275	300
Time of the 2nd desorption (td2) (min)	20	25	30
Focusing trap (Aft)	Tenax-TA	*	TA-CX-CS

* The two types of adsorbents were tested at the central point

Preconcentration of the samples

The preconcentration of the organic contaminants of VCM was performed in glass tubes, filled with two types of solid adsorbents: 60:80 mesh Tenax-TA™ (6 mm O. D., 4 mm I. D., 4.5” length) and 20:35 mesh Tenax-TA™/60:80 mesh Carboxen™ 1000/60:80 mesh Carbosieve™ SIII (6 mm O. D., 4 mm I. D., 4.5” length). After a multivariate optimization for both adsorbents, the VCM was purged at 20 mL min^{-1} to complete a sampled volume of 1.5 L (Figure 1). While Tenax-TA was more effective in the retention of non-polar compounds or compounds with moderately long chains (C6 – C30), Tenax-TA/Carboxen1000/CarbosieveSIII was more efficient in retaining polar or light compounds (C2 – C6).

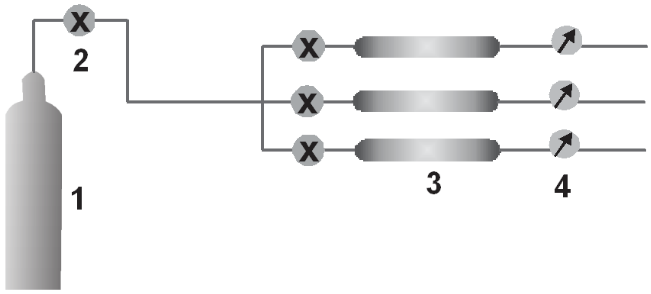

Figure 1 – Preconcentration system for organic contaminants in VCM: (1) steel cylinder containing pressurized VCM; (2) flow control valve; (3) adsorbent tubes; (4) flow meter

Thermal desorption

Thermal desorption was performed in a Dynatherm Thermal Desorption Autosampler – TDA system (CDS Analytical, Inc) coupled to a GC-MS system. Two steps were carried out to transfer the compounds retained in the adsorbents to the GC-MS system, the first involving desorption of the sampled adsorbent to the focusing trap and the second involving desorption of the focusing trap to the chromatographic column.

Thermal desorption of Tenax-TA

The optimized desorption conditions for Tenax-TA were: desorption to the focusing trap (60:80 mesh Tenax-TA; 6 mm O. D., 0.9 mm I. D., 4.5” length) at 280ºC for 20 min with He at 80 mL min^{-1} and the transfer line at 250ºC, followed by desorption of the focusing trap to the GC column at 300ºC for 15 min and the transfer line at 250ºC.

Thermal desorption of Tenax-TA/Carboxen1000/CarbosieveSIII

The optimized desorption conditions for Tenax-TA/Carboxen1000/CarbosieveSIII were: desorption to the focusing trap (60:80 mesh Tenax-TA / 60:80 mesh Carboxen 1000 / 60:80 mesh Carbosieve SIII; 6 mm O. D., 0.9 mm I. D., 4.5" length) at 320ºC for 20 min with He at 80 mL min^{-1} and the transfer line at 250ºC, followed by desorption of the focusing trap to the GC column at 270ºC for 20 min and the transfer line at 250ºC.

Before the first use and between samplings, the adsorbents were conditioned by heating them to 280ºC for 30 min with nitrogen at 100 mL min^{-1}, using a Dynatherm 9300 ACEM Automated Concentrating Environmental Monitor (CDS Analytical, Inc).

GC-MS analyses

The GC-MS analyses were performed in a gas chromatograph (Varian 431-GC) coupled to a mass spectrometer (Varian 200-MS IT) using a CP-PoraBOND Q capillary column (25 m × 0.25 mm × 3 µm, 100% divinylbenzene; Varian). The column oven program was 30 ºC (4 min) – 6 ºC min^{-1} – 130 ºC – 10 ºC min^{-1} – 300 ºC (4 min), keeping the carrier gas flow (helium) in the column at 1.0 mL min^{-1} and the injector at 250 ºC with a split ratio of 10:1. The mass spectrometer operated in electron impact (EI) ionization mode and full scan in the range of m/z 50–350, the trap at 220 ºC, the manifold at 50 ºC, and the transfer line at 280 ºC. The substances were identified by analyzing their mass spectra and by comparing the spectra obtained with those of the NIST virtual library, and a minimum similarity of 80% was considered for acceptance of the compounds identified in the chromatograms.

Multivariate statistical analysis

The Principal Component Analysis (PCA) was performed using Statistica 7.0 software (StatSoft, Inc), and the statistical treatment was performed on the data of the integrated chromatographic peak areas of the identified contaminants. The samples were considered as cases and the contaminants as variables.

Results and Discussion

Optimization of adsorption

Figures 2 and 3 show that the factors flow and volume, as well as the interaction between them, were significant in the adsorption preconcentration of both adsorbents. In both cases, the flow rate effect was negative, indicating an increase in the analytical response with the decrease from the upper to the lower level, since the residence time of the analytes as they pass through the adsorbent bed increases. On the other hand, the effect of volume was positive, indicating an increase in the analytical response with the increase in sample volume. However, the maximum sample volume is limited by the retention capacity of the adsorbent's active sites, making it necessary to determine the breakthrough volume for the conditions of the experiments. Lastly, the flow/volume interaction showed a negative effect.

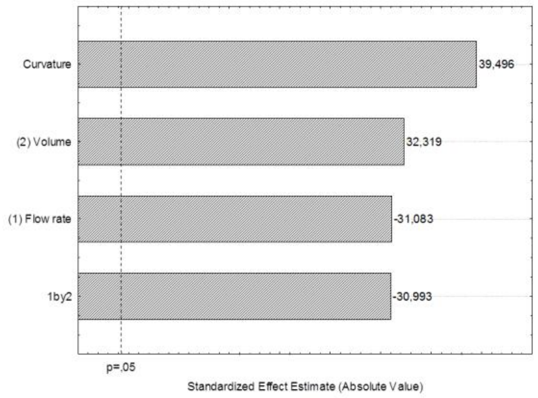

Figure 2 – Pareto chart of the factors flow, volume and flow/volume interaction, for adsorption preconcentration on Tenax-TA

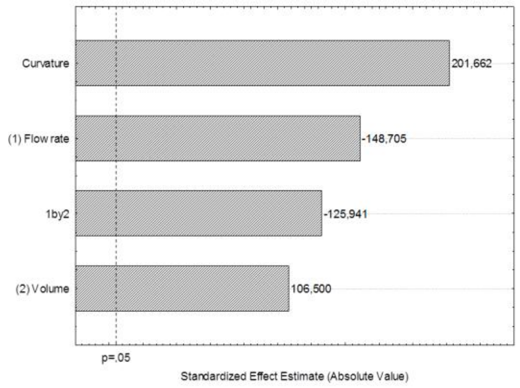

Figure 3 – Pareto chart of the factors flow, volume and flow/volume interaction, for adsorption preconcentration on Tenax-TA/Carboxen1000/CarbosieveSIII

The response surfaces for Tenax-TA (Figure 4) and Tenax-TA/Carboxen1000/ CarbosieveSIII (Figure 5) show the tendency of the sum of the total peak area of adsorbed compounds as a function of flow and volume. The region of the experimental domain under study, in which the highest analytical response was found, is about 20 mL min^{-1} for flow, and 2.0 L for sample volume. However, some samples showed a breakthrough starting from 1.5 L in different sampling periods, which was a limiting factor. Thus, the selected conditions for the preconcentration procedure, in both cases, were 20 mL min^{-1} for flow and 1.5 L for the final sample volume.

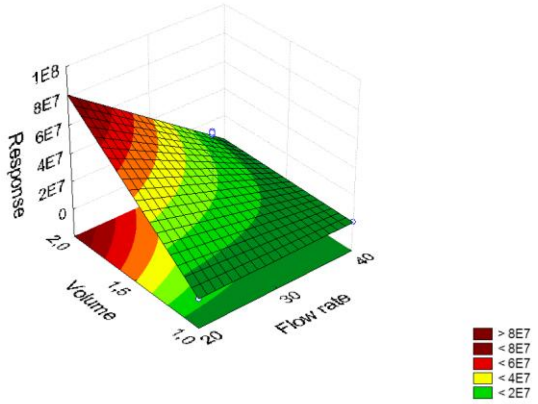

Figure 4 – Response surface of adsorption on Tenax-TA

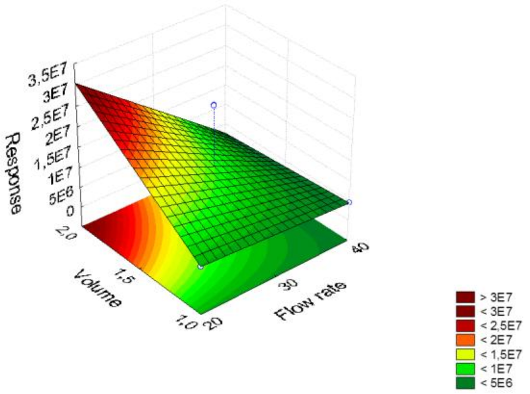

Figure 5 – Response surface of adsorption on Tenax-TA/Carboxen1000/CarbosieveSIII

The sample flow proved to be very important for adsorption, because of its direct influence on the residence time of the analytes in the adsorbent bed, on the amount of analyte molecules that compete for an active site per unit of time and on the pressure on the adsorbent bed. The total area of the chromatographic peaks of adsorbed compounds was higher at the lowest flow, indicating maximization of the influence of the parameter residence time. On the other hand, the sample's volume was the first most influential factor in Tenax-TA adsorption and the third most influential factor in Tenax-TA/Carboxen1000/ CarbosieveSIII adsorption. The breakthrough volume for a given adsorbent may vary with its surface area, and with the balance of the interaction forces between adsorbent and analytes and between adsorbent and interferents, such as moisture. Tenax-TA has a relatively small surface area, but it is hydrophobic. On the other hand, Tenax-TA/Carboxen1000/CarbosieveSIII has a relatively larger surface area, but has a strong affinity for water, due to the presence of active carbon (Carboxen1000) and the carbon-based molecular sieve (CarbosieveSIII), whose structures contain polar groups.

Optimization of the thermal desorption method

Thermal desorption of Tenax-TA

The Pareto chart in Figure 6 shows that all the factors were significant at a 95% confidence interval ($p<0.05$). The response points out to a maximum value for the upper levels of the desorption temperatures and the desorption flow. On the other hand, lower values of desorption time tend to maximize the response.

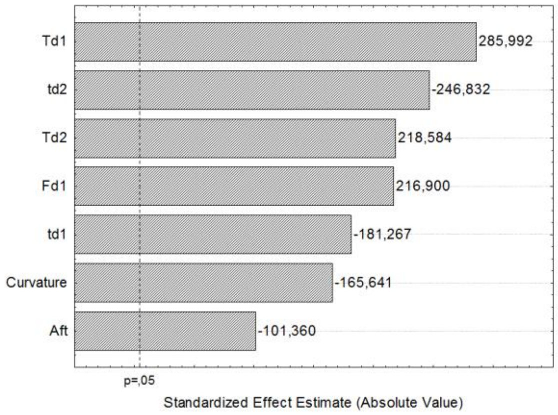

Figure 6 – Pareto chart of the effects of the factors evaluated in the thermal desorption of Tenax-TA, based on the $2^{(6-2)}$ design

After initial screening of the significant factors, a $2^{(5-2)}$ fractional factorial design was generated with three replications at the central point, making a total of eleven experiments, as described in Table 3.

Table 3 – Levels of the factors of the $2^{(5-2)}$ fractional factorial design for thermal desorption of Tenax-TA

Factor	-1	0	+1
Temperature of the 1st desorption (Td1) (°C)	280	300	320
Time of the 1st desorption (td1) (min)	10	15	20
Desorption flow (Fd1) (mL min^{-1})	40	60	80
Temperature of the 2nd desorption (Td2) (°C)	280	300	320
Time of the 2nd desorption (td2) (min)	10	15	20

The Pareto chart in Figure 7 shows that, at 95% confidence, only three of the five evaluated factors remained significant: 1st desorption temperature, 1st desorption time and desorption flow, with the first one pointing to the minimum value and the other two to the maximum values. Thus, the optimized values of the 1st desorption time and flow were, respectively, 20 min and 80 mL min^{-1} while the 1st desorption temperature was set at 280ºC. Moreover, the values of the factors that were not significant were set at the central point, since the curvature was significant.

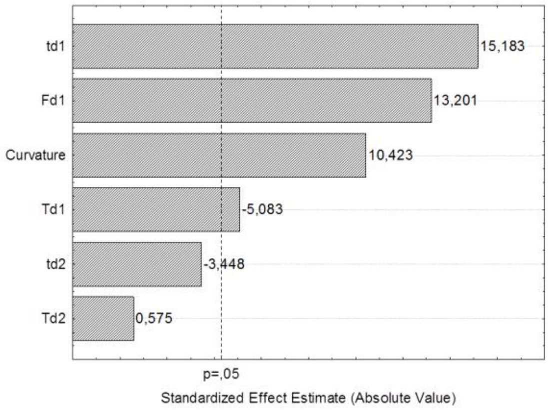

Figure 7 – Pareto chart of the effects of the factors for the thermal desorption of Tenax-TA, based on the $2^{(5-2)}$ design

Comparing the factorial planning $2^{(6-2)}$ (Figure 6) with the $2^{(5-2)}$ planning (Figure 7), it can be seen that there was a reduction in the amount of significant factors, from five to three, together with a minimization on its effects, showing that the optimization of the thermal desorption parameters led to an improvement in the method. Figure 7 also shows that, once the parameters levels were modified, the effects of the 1st desorption time and 1st desorption temperature had undergone an inversion in their trends, now pointing, respectively, to their maximum and minimum values. The optimized conditions for the thermal desorption of the contaminants of VCM adsorbed on Tenax-TA are described in Table 4.

Table 4 – Optimized values of the parameters of thermal desorption on Tenax-TA

Parameter	Optimized value
Temperature of the 1st desorption (°C)	280
Time of the 1st desorption (min)	20
Desorption flow (mL min^{-1})	80
Temperature of the 2nd desorption (°C)	300
Time of the 2nd desorption (min)	15
Focusing trap	Tenax-TA

Thermal desorption of Tenax-TA/Carboxen1000/CarbosieveSIII (TA-CX-CS)

As described above, the thermal desorption of the compounds retained in TA-CX-CS was assessed using a $2^{(6-2)}$ fractional factorial design with the same six factors and levels shown in Table 2. The Pareto chart in Figure 8 shows that the temperature of the 1st desorption, the desorption flow, and the type of focusing trap (TA-CX-CS) led to an increase in the peak area of the desorbed compounds at the upper level of these factors. On the other hand, the temperature of the 2nd desorption and the time of 1st and of 2nd desorption led to an increase in the peak area of the desorbed compounds at the lower level of these factors.

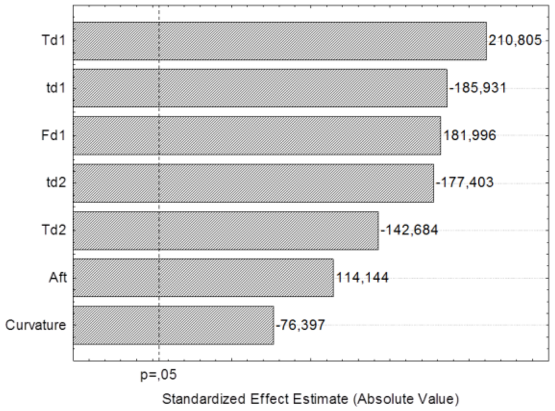

Figure 8 – Pareto chart of the effects of the factors on the thermal desorption of the TA-CX-CS adsorbent, based on the $2^{(6-2)}$ design

Figures 6 and 8 show that Td2 has opponent effects for Tenax-TA and TA-CX-CS sorbents. While in the first case an increase in this parameter would also result in an increase in the peak areas, in the second case there would be a decrease. The other parameters have similar effects for both sorbents.

To optimize the remaining five significant factors, a $2^{(5-2)}$ fractional factorial design was performed, with three replications at the central point, making a total of eleven experiments. Table 5 lists the values of the levels of the factors.

Table 5 – Levels of the factors of the $2^{(5-2)}$ fractional factorial design for thermal desorption of the TA-CX-CS adsorbent

Factor	-1	0	+1
Temperature of the 1st desorption (Td1) (°C)	280	300	320
Time of the 1st desorption (td1) (min)	10	15	20
Desorption flow (Fd1) (mL min^{-1})	40	60	80
Temperature of the 2nd desorption (Td2) (°C)	230	250	270
Time of the 2nd desorption (td2) (min)	10	15	20

The Pareto chart in Figure 9 shows, once again, that only three of the five evaluated factors remained significant at 95% of confidence, two of them (td1 and Td1) as we had already seen also for Tenax-TA (Figure 7). The 1st and 2nd desorption temperatures and the 1st desorption time caused the response to increase to the upper levels of these factors, 320ºC, 270ºC and 20 min, respectively. The values of the factors that were not significant, were set at the upper level, since the experiment in which the peak area of the desorbed compounds was the highest presented these conditions. Therefore, the flow was set at 80 mL/min and the time of the 2nd desorption in 20 min.

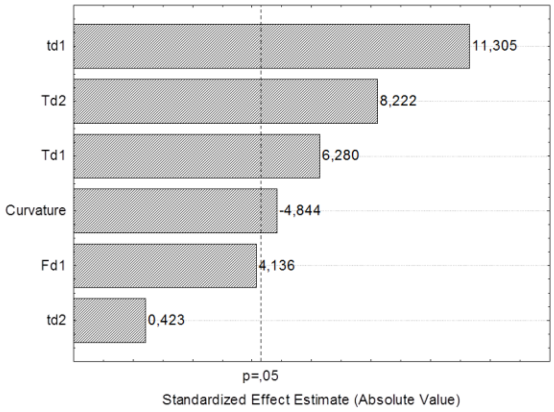

Figure 9 – Pareto chart of the effects of the factors on the thermal desorption of the TA-CX-CS adsorbent, based on the $2^{(5-2)}$ design

Comparing the factorial planning $2^{(6-2)}$ (Figure 8) with the $2^{(5-2)}$ planning (Figure 9), it can be seen that there was a reduction in the amount of significant factors, from five to three, together with a minimization of its effects, showing that the optimization of the thermal desorption parameters led to an improvement in the method. Figure 9 also shows that, once the other parameters were modified, the effect of the 1st desorption time and the 2nd desorption temperature had undergone an inversion in their trends, now pointing to their upper levels. The optimized conditions for the thermal desorption of the contaminants of VCM adsorbed on Tenax-TA/Carboxen1000/CarbosieveSIII are described in Table 6.

Table 6 – Optimized values of the parameters of thermal desorption on TA-CX-CS

Parameter	Optimized value
Temperature of the 1st desorption (°C)	320
Time of the 1st desorption (min)	20
Desorption flow (mL min^{-1})	80
Temperature of the 2nd desorption (°C)	270
Time of the 2nd desorption (min)	20
Adsorbent focusing trap	Tenax-TA/Carboxen1000/CarbosieveSIII

Identification of the organic contaminants of VCM in different stages of the process

The VCM collected at different stages of the process during the year 2012 was analyzed to identify the contaminants, compare their profiles of relative abundance, and check for possible differences in the samples, by examining the clusters in Principal Components Analysis. The contaminants considered for each point were those identified in all the samples collected at that point. Figure 10 depicts a typical chromatogram obtained in the analysis of the VCM in the spherical storage tank.

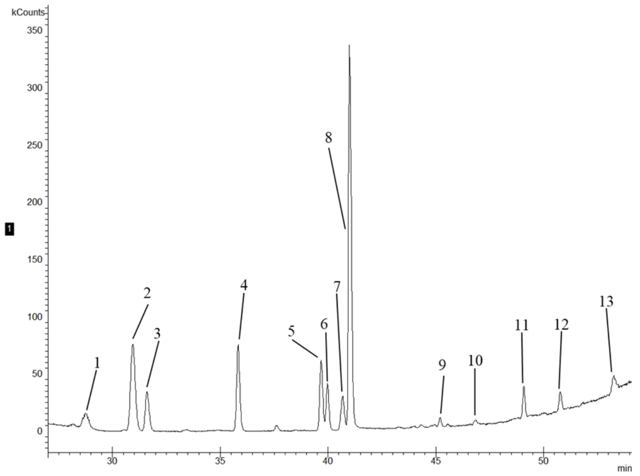

Figure 10 – Characteristic GC-MS chromatogram of a VCM sample from point D (spherical tank). Contaminants were preconcentrated on Tenax-TA (20 mL min^{-1} flow rate and 1.5 L final sample volume) and desorbed according to conditions on Table 4.
(1) trichloromethane, (2) benzene, (3) 1,2-dichloroethane, (4) toluene, (5) ethylbenzene, (6) o-xylene, (7) p-xylene, (8) styrene, (9) 1-octanol, (10) phenol, (11) chloroacetophenone, (12) acetophenone and (13) naphthalene.

As mentioned earlier, the VCM samples were collected at four points in the plant, as indicated in Figure 11, namely: Point C – fresh VCM from the distillation tower; Point D – VCM in the spherical storage tank; Point B – VCM at the inlet of the polymerization reactor (mixture of VCM from the spherical tank and VCM recovered from the polymerization reactor); Point A – unreacted VCM recovered at the outlet of the polymerization reactor.

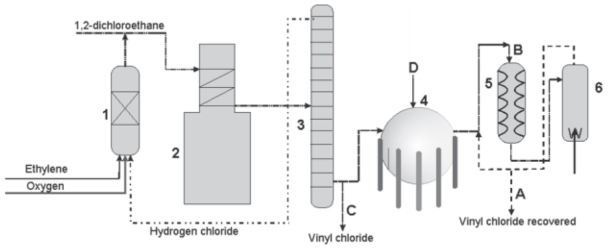

Figure 11 – Simplified diagram of the stages of the production, storage and recovery process of vinyl chloride monomer and of the sample collection points. (1) ethylene oxychlorination reactor; (2) 1,2-DCE pyrolysis furnace; (3) distillation tower which separates HCl and VCM; (4) VCM spherical storage tank; (5) VCM polymerization reactor; (6) PVC purification post-reactor; (A) unreacted recovered VCM; (B) VCM from the spherical tank + recovered VCM; (C) fresh VCM; (D) VCM from the spherical tank

The analyses revealed a total of 29 identified compounds, of which 19 were present in all the samples of at least one of the monitored points. These compounds were thus selected for this study and are described in Table 7. A total of 12 contaminants were found in samples of fresh

VCM from the distillation tower (point C) and at the inlet of the polymerization reactor (point B), while 13 contaminants were found in samples of VCM from the spherical tank (D), and 16 in samples of VCM recovered at the exit of the polymerization reactor (point A). The fact that only 12 contaminants were detected in the mixture of VCM from the spherical tank and recovered VCM (point B) was probably the result of a dilution effect of the stream, given that the proportion of recovered VCM in the mixture varied by up to 20%.

The other 10 contaminants, not considered in this work since they were not identified in, at least, all samples for a same collection point, were chloromethane, chloroethane, 1,1-dichloroethane, 1,1,2-trichloroethane, chlorobenzene, acenaphthene, decane, dodecane, tridecane and 1,2,4-trimethylbenzene.

Table 7 – Contaminants of VCM found in different stages of the process

Contaminant	VCM at the distillation tower (Point C)	VCM from the spherical storage tank (Point D)	VCM at the reactor inlet (Point B)	VCM recovered at the reactor outlet (Point A)
1,3-Butadiene			x	x
Benzene	x	x	x	x
2,4-Hexadiene				x
Toluene	x	x	x	x
1-Octanol	x	x	x	x
Ethylbenzene	x	x	x	x
o-Xylene	x	x	x	x
p-Xylene	x	x	x	x
Styrene	x	x	x	x
Propylbenzene				x
1,4-Diclorobenzene				x
Chloroacetophenone	x	x		x
Propenylbenzene				x
Phenol	x	x	x	x
Acetophenone	x	x		x
Naphthalene	x	x	x	x
1,2-Dichloroethane	x	x	x	
Trichloromethane		x		
Benzaldehyde			x	

Fresh VCM (Point C)

Twelve contaminants were identified in the virgin VCM collected at the exit of the distillation tower, from a total of five analyzed samples. These contaminants were 1,2-dichloroethane, styrene, benzene, 1-octanol, toluene, chloroacetophenone, ethylbenzene, naphthalene, p-xylene, o-xylene, acetophenone and phenol. The abundance profile of the contaminants was calculated, based on the average of the peak areas of the compounds in the chromatograms and normalized to the one that presented the highest average area. The 1,2-dichloroethane showed the highest abundance, probably because it is the raw material entering the pyrolysis furnace for the production of VCM in the plant, and because its complete removal is difficult, even after successive VCM purification steps. Styrene, which showed the second highest relative abundance, may have formed during the pyrolysis step, from the dehydrogenation of ethylbenzene, which was also identified in the sample. In addition to this proposal, it is also possible that part of the benzene and styrene were already present, as impurities originating from the ethylene used as the starting raw material. It was still not possible to identify a likely source of the 1-octanol, an impurity that showed the fourth highest relative abundance. As for the aromatic hydrocarbons toluene, ethylbenzene, naphthalene, p-xylene and o-xylene, they may have come from ethylene, the starting raw material of the process, or have been generated in the DCE pyrolysis step. However, they were present in lower relative abundances, suggesting that most of them may have been removed in one of the VCM purification steps. Acetophenone, on the other hand, may be a product of ethylbenzene oxidation, and chloroacetophenone a product of ethylbenzene chlorination and oxidation. Lastly, phenol may be a product of benzene oxidation in the oxychlorination step.

VCM in the spherical storage tank (Point D)

After DCE and HCl are separated from the VCM, it undergoes a neutralization step of residual HCl with caustic soda, and then treated with an antipolymerizer and stored in the spherical tank. At this point, 13 contaminants were identified in four samples, namely styrene, toluene, benzene, p-xylene, o-xylene, ethylbenzene, naphthalene, 1,2-dichloroethane, trichloromethane, chloroacetophenone, acetophenone, 1-octanol and phenol. With the exception of trichloromethane, the others had already been identified in the VCM at the outlet from the distillation tower. The normalized abundance profile calculated shows that the three contaminants with the highest average relative abundance were styrene, toluene and benzene, suggesting that they originate from the same source or process, such as the ethylene or the DCE pyrolysis reaction. Considering that VCM in the spherical tank must be specified in terms of its organic contaminants, before it undergoes the polymerization reaction, it is important to draw attention to styrene, which is reported in the literature as a potent inhibitor of VCM polymerization.

VCM at the inlet of the polymerization reactors (point B)

When VCM temporarily stored in the sphere exits this storage tank, it receives the addition of recovered VCM and is then sent to the polymerization reactors. Twelve substances identified as contaminants were found in five samples of this VCM, namely styrene, benzene, 1,2-dichloroethane, ethylbenzene, toluene, o-xylene, p-xylene, 1-octanol, 1,3-butadiene, naphthalene, benzaldehyde and phenol. As in the VCM in the spherical tank, the contaminant that presented the highest relative abundance was styrene. It is important to highlight the presence of 1,3-butadiene and benzaldehyde in all samples. 1,3-butadiene was also identified in the recovered VCM (point A), its probable source since this VCM is mixed with that which comes from the spherical tank, before point B. It is noteworthy that 1,3-butadiene is reported in the literature as a strong inhibitor of VCM polymerization.

It was also found that, although chloroacetophenone and acetophenone have been identified in all the analyzed samples from points A (recovered VCM) and D (spherical storage tank), neither of the two contaminants were identified at point B, despite the VCM at this point is the result of the mixture of VCM from both. This is possibly due to their presence below the detection limits of the method.

Recovered VCM (point A)

After polymerization, the unreacted VCM from previous batches is recovered and distilled to remove the additives used in polymerization. Figure 15 shows the normalized abundance profile. Sixteen contaminants were identified in the four analyzed samples, namely benzene, styrene, ethylbenzene, toluene, 1,3-butadiene, o-xylene, p-xylene, chloroacetophenone, acetophenone, 1,4-dichlorobenzene, naphthalene, 1-octanol, phenol, propylbenzene, 2,4-hexadiene and propenylbenzene. Some contaminants that were not identified in samples collected at the other points, such as 2,4-hexadiene, 1,4-dichlorobenzene, propenylbenzene and propylbenzene, were identified at this point, albeit at low relative abundances. These contaminants can be formed through reactions involving not only the substances already present in VCM, such as benzene, DCE and VCM itself but also the additives of polymerization or their impurities in the reaction medium. In addition to the aforementioned styrene and 1,3-butadiene, 2,4-hexadiene has also been reported in the literature as a moderate inhibitor of VCM polymerization.

Figure 12 shows that nine contaminants, comprising seven aromatic hydrocarbons, an alcohol and phenol, were identified in all the 18 analyzed samples taken from the various collection points. Unlike chlorinated and carbonyl compounds, few studies in the literature focus on the effect of aromatic hydrocarbons on the polymerization reaction of VCM and on the properties of PVC. Considering the industrial process in question and the reactions involved in the production of VCM, it is likely that the main source of these contaminants should be the ethylene, which feeds the oxychlorination reactor for the production of 1,2-DCE, and also possible pyrolysis and cyclization reactions in the 1,2-DCE pyrolysis furnace.

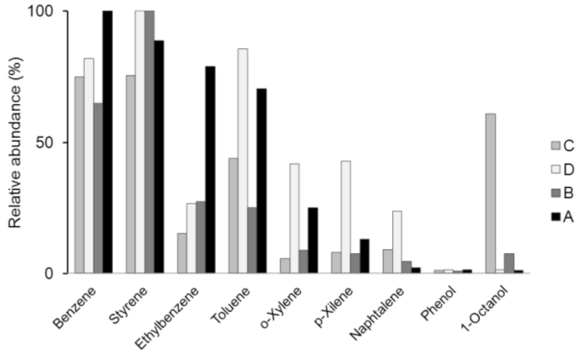

Figure 12 – Relative abundances of the VCM contaminants as a function of the sampling point. A- recovered VCM; B- VCM at the polymerization reactor inlet; C- VCM at the distillation tower outlet; D- VCM in the spherical tank

Principal Components Analysis (PCA)

The principal component analysis (PCA) was performed using a data set corresponding to the peak area of the nineteen compounds identified in the chromatograms of the eighteen analyzed samples. The correlation matrix for PCA multivariate analysis was chosen because it excludes the effect of different scales of the variables. The contaminants of VCM were considered as variables and the samples as cases of the multivariate analysis.

The score graph of the samples in Figure 13 indicates their separation into three distinct clusters. Cluster I contains the samples with negative scores in PC1, while clusters II and III contain the samples with positive scores. On the other hand, PC2 was able to separate clusters II and III, which presented negative and positive scores, respectively. The greatest discrimination along PC1 was observed among samples of VCM recovered after polymerization (point A, cluster I), samples of VCM from the distillation tower (point C, cluster II), and VCM from the spherical tank plus VCM in mixtures of spherical tank and recovered VCM (points D and B, cluster III), with 50.69% of the total variance. On the other hand, the samples of VCM from point C and VCM from points D and B differed with less variability along PC2, with 17.29% of the total variance. The first two components (PC1 and PC2) explain 68% of the total variance of the samples taken from the different points of the VCM process.

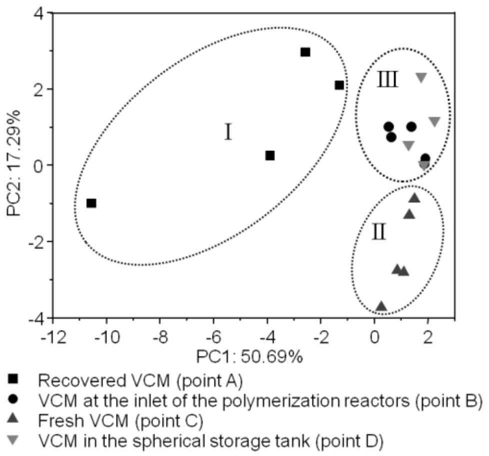

Figure 13 – Principal components analysis (PC1 x PC2) of VCM samples collected at different points of the process

Figure 14 shows the score graph of the VCM contaminants, indicating those that are correlated and which contributed to the variability of the samples. The contaminants with characteristic vectors located to the left of the origin of factor 1 contributed to the variability of the samples of recovered VCM (point A), among which the eleven with the highest weights were seven aromatic hydrocarbons, plus 1,3- butadiene, 1,4-dichlorobenzene, acetophenone and phenol. On the other hand, 1,2-dichloroethane, 1-octanol, benzaldehyde and trichloromethane contributed with a higher weight to the discrimination of the samples of VCM from the distillation tower (point C) and VCM from the spherical tank (point D) plus VCM in mixtures of spherical tank and recovered VCM (point B). In the case of point C, the probable main factor that caused 1,2-dichloroethane and 1-octanol to act as principal discriminators was their presence in higher relative abundances at this point when compared to the others. As for points B and D, benzaldehyde and trichloromethane were good discriminators because each of them was present only at these points.

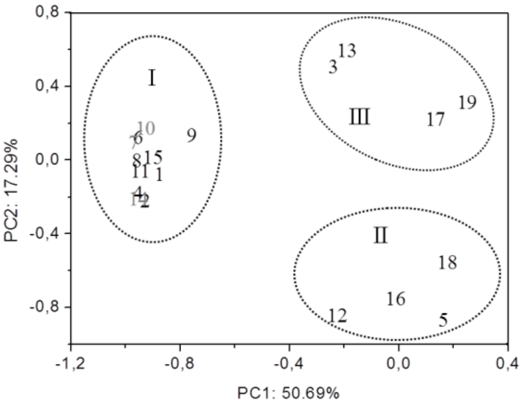

Figure 14 – Principal components analysis (PC1 x PC2) of VCM contaminants identified at the different points of the process. (1) 1,3-Butadiene, (2) Benzene, (3) 2,4-Hexadiene, (4) Toluene, (5) 1-Octanol, (6) Ethylbenzene, (7) o-Xylene, (8) p-Xylene, (9) Styrene, (10) Propylbenzene, (11) 1,4-Dichlorobenzene, (12) Chloroacetophenone, (13) Propenylbenzene, (14) Phenol, (15) Acetophenone, (16) Naphtalene, (17) Benzaldeyde, (18) 1,2-Dichloroethane, (19) Trichloromethane.

Conclusions

The analytical method developed in this work, based on TD-GC-MS, has shown that Tenax – TA and Tenax-TA/Carboxen1000/CarbosieveSIII (TA-CX-CS) sorbents, used in the pre-concentration of the samples, were able to work in a complementary manner. While the first one was more effective in the retention of non-polar and moderately long chains compounds, the second was more effective in retaining polar or light compounds.

When applied in the analysis of VCM, originating from the production, storage and recovery stages in an industrial PVC production plant, the developed and optimized method successfully identified twenty nine organic contaminants in this monomer, nineteen of which were present in all the samples from at least one of the four monitored points. The VCM collected at the exit of the polymerization reactor showed the largest number of identified substances, i.e., a total of sixteen.

Among the 19 contaminants, 1,2-dichloroethane, styrene and benzene were the ones that presented the highest relative abundances in the VCM collected, respectively, at the exit of the distillation tower, in the spherical storage tank, and at the inlet and outlet of the polymerization reactor. Nine contaminants were identified as present at all the four points, i.e., seven aromatic hydrocarbons, an alcohol and phenol, suggesting that their main source is the ethylene fed into the chlorination reactor, as well as possible pyrolysis and cyclization reactions in the 1,2-EDC pyrolysis furnace.

Among the identified contaminants, it is worth noting styrene, 1,3-butadiene and 2,4-hexadiene, which are cited in the literature as inhibitors of VCM polymerization.

The principal components analysis was successful in distinguishing the differences in the composition of VCM collected at each of the four sampling points, and based on this identification, separate them into three distinct clusters, in addition to identifying the main compounds in each cluster responsible for the differences.

Considering that the control of the purity of the VCM monomer is critical to the quality of the PVC produced, although the impurities were not quantified in this work, it contributes to bring information concerning the identification of contaminants and their distribution profile, in VCM monomer coming from different points of an industrial plant. This information should serve as an input, to guide actions for indicating points where greater control and corrective measures are required to ensure the quality of manufactured PVC.

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