Reviewer 1:

First of all, we would like to acknowledge the comments provided by Reviewer#1, which have help us improve our manuscript. Clarifications of the issues below have been included in the MS.

Line 18.- Is there is an official recommendation? – Please provide a reference

Thanks for the advice. The official recommendation is EN 14662 Standard. Ambient air - Standard method for the measurement of benzene concentrations - Part 3: Automated pumped sampling with in situ gas chromatography, 2015. However, we have decided to eliminate the complete sentence from the Abstract as it is not relevant.

Line 33.- Please be more pragmatic in the resolution of this problem. Apart from requesting the manufacture intervention, it would be useful to present a list of measurements to carry out by the user in order to minimize or avoid this problem.

We appreciate the suggestion from the reviewer. This matter has been clarified in the MS: we have added information in the Result and Discussion section about measurements to carry out by the user in order to minimize this problem. The final wording is "[…] *This approach would require continuous measurements of TCM in air and a knowledge of how TCM deviates measurements from its real value, which in turn, requires carrying out tests similar to those presented in this paper with dynamic dilution systems in controlled test atmospheres. This measure could not be easy to apply for economic and technical reasons so the whole responsibility must not only fall on the network managers. It seems reasonable that the manufacturers of the equipment tackle actions for solving this problem –or, at least, for reducing the extent of the interference in their measurements-, since they have the required technology and equipment. In any case, users of this type of equipment should be aware of the problem to try to minimise it. The discussion of this issue in the appropriate forum (e.g. the European Committee for Standardisation) seems also pivotal to reduce the uncertainty in benzene measurements by GC-PID in presence of TCM concentrations*".

Line 49/50.- change degrees to ºC:

It has been done. Thank you for your suggestion.

Line 59.- Remove double endpoint

Double endpoint has been deleted. Thank you for your recommendation.

Line 70.- Why is it compared with hydrocarbons of similar molecular weight? This is not an indicator of stability in the atmosphere

Thank you for this interesting comment. We agree with the reviewer and accordingly, the mention to hydrocarbons of similar molecular weight has been removed. It was a comment recommended by a previous journal reviewer.

Line 76 .- Please make reference to the corresponding legislation

We have added the reference: Directive 2008/50/EC of the European Parliament and of the Council of 21 May 2008 on ambient air quality and cleaner air for Europe, Off. J. Eur. Communities, 152, 1–43.

http://eurlex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2008:152:0001:0044:EN:PDF

Line 127.- Please provide appropriated reference.

Thank you for your suggestion. The following reference has been added: Senum, G. I.: Quenching or enhancement of the response of the photoionization detector, J. Chromatogr. A, 205(2), 413–418, doi:10.1016/S0021-9673(00)82668-0, 1981.

Line 223.- Who was the certifying body?

We appreciate the suggestion from the reviewer; we have included in the MS the certifying bodies, which were the respective manufacturers of the gas mixtures. The mixtures were certified according to Standard ISO 6141:2000.

What are the uncertainties of the final generated concentrations?

This is an interesting point. Flow rates were continuously controlled and the expanded uncertainty of the generated concentrations was calculated from the standard uncertainty of the gas mixtures in the gas cylinders and the standard uncertainties of the flow rates. We have added a new paragraph in the Experimental set-up section: "*The expanded uncertainties of all generated concentrations of pollutants were estimated from the standard uncertainties of the high concentration gas cylinders and the standard uncertainties of the gas flow rates. In all cases, the final expanded* *uncertainty was less than 5%, according to the limit established in Standard EN 14662-3*".

Line 356.- This seems a relevant item to be reported in the conclusions to be considered in the EN standard.

We agree with the reviewer. We have modified the Conclusion section accordingly: "The research described in this article has determined that TCM causes a significant interference in the measurement of benzene by GC-PID. This interference is negative, that is, readings of benzene are below their real ambient values, which may originates a mismanagement of the air quality of a location with presence of TCM in its air in relation to benzene".

Line 474.- Although these biases seem very high, it would be of interest to demonstrate that they are significant compared to the measurement uncertainties by considering the whole experimental setup.

As stated before, the uncertainty of the generated gas mixtures was below 5%. In addition, a lack-of-fit test was performed in order to test the accuracy of the readings. For this, after calibration of the analysers, several gas mixtures of benzene in air with different concentrations ranging from 0 to 50 $\mu g/m^3$ were measured. Relative differences between the readings and the reference concentrations were calculated and, in all cases, were below 10%. This value is much lower than the biases that occur in the readings when there is TCM in air ambient (34, 44 and 70 % when there is a TCM concentration of 0.7, 1.4 and 4.5 $\mu g/m^3$). Moreover, other potential influencing parameters such as temperature or pressure were kept constant during the experiments, allowing to conclude that the high biases obtained in readings when TCM was added to the mixture are due to the presence of this substance. The following paragraph has been included in the MS: "*In order to ensure that the biases obtained in these and subsequent experiments were only due to the interfering compounds tested, sample and surrounding temperatures, sample pressure and voltage were kept constant during all experiments. A lack-of-fit test was performed in order to test the accuracy of the readings. For this, after calibration of the analysers, several gas mixtures of benzene in air with different concentrations ranging from 0 to 50 $\mu g/m^3$ were measured. Relative differences between the readings and the reference concentrations were calculated and, in all cases, were below 10%, much lower than the values reported in the Result and Discussion section*".

Line 486 .- Please consider my comments on L33:

We have added a new paragraph in the "Results and discussion section" (please see comment on line 33): Also, in "Conclusions" we have added a similar conclusion. The final wording is the following: "*Interestingly enough, it is established in part 3 of the standard EN 14662:2015 that the managers of the air quality monitoring network are responsible for determining the presence of TCM in the area where benzene is measured. If detected, they must act to eliminate the effect of the interferent. However, this approach would require continuous measurements of TCM in air and a knowledge of how TCM deviates measurements from its real value, which in turn, requires carrying out tests similar to those presented in this paper with dynamic dilution systems in controlled test atmospheres. This may entail economic and technical issues so manufacturers of the chromatographs should try to solve this problem as they have greater technical and scientific capacity than network managers. In any case, all these issues should be discussed in the appropriate forum (e.g. the European Committee for Standardisation) in order to improve the uncertainty of benzene measurements and, thus, the management of the air quality*".

Line 614.- Why are Ucorg and Vtest (%) reported only in this Table?

Parameters U_{Corg} and V_{test} (%) were only reported in Table 3 because this table contained the data obtained according to concrete indications of the EN 14662 Standard, which requires the calculation of V_{test} and U_{Corg} in order to compare and verify its acceptability with the performance criterion (<5%) established in such standard.

We consider that using the relative error is more logical and useful to evaluate the deviations than the V_{test} and U_{Corg} parameters. For this reason, in the rest of the Tables, which contained results of tests proposed by ourselves and not contemplated in the Standard, such parameters were not included (U_{Corg} and V_{test}). However, we have decided to merge former Tables 3 and 4 into a single new table (Table 2) in order to save space, and we have decided to calculate parameters V_{test} and U_{Corg} for the results presented in former Table 4 to maintain the symmetry of new Table 2.

Line 649.- Why are the results of analyzer II not reported?

The Analyzer II belongs to the official surveillance network from the Government of Región de Murcia and it is operating continuously in a monitoring station. Therefore, we only had such equipment for a limited time in our lab. Given that both analysers exhibited a similar performance in the first set of experiments carried out, we considered that the results obtained with Analyser I would be representative of both of them. In addition, a reproducibility test was carried out in the lab. Both analysers were subject to measure simultaneously a gas mixture containing 5 μg/m^3 nominal benzene in zero air. The reproducibility (in μg/m^3) was calculated as:

$$Reproducibility = \sqrt{\frac{\sum d_i^2}{2n}}$$

where d_i is the *i* difference in readings between Analyser I and II and *n* is the total number of measurements (6 in our case). The value obtained was 0.067 μg/m^3 when the average concentration of benzene in the reference gas mixture gas 4.6 μg/m^3, which means 1.5% bias. This value was considered low enough to perform the subsequent tests just with one analyser. All these results have been added to the MS.

Line 470 and 649.- What is the reproducibility of the Eq (15) between different analyzers?

Eq. (15) was only obtained for Analyser I, as only this analyser was subject to the tests in Section 2.2.2. Reproducibility has been calculated as detailed in the previous comment.

Comments to Reviewer#3

This manuscript discusses possible interferences in the measurements of benzene using a European Standard method. The manuscript fits in AMT topic wise. There are no errors in the manuscript but it is a report rather than a scientific manuscript. The manuscript needs to be substantially restructured and reformatted to even fit the instructions for AMT (See https://www.atmospheric-measurement-techniques.net/for_authors/manuscript_preparation.html) especially in regards to sections. The manuscript preparation also lacks attention to detail and is sloppy. The present webpublished version has randomly underlined sections, which might be track changes from previous editing. This is very sloppy and together with numerous typos, one can only hope the authors performed their scientific work more carefully than the preparation of their manuscript.

First of all, we the authors would like to apologise for the original manuscript. It is true that was sloppy and there was much room for improvement. We did misregard its format (though not its content) because we had an internal deadline to meet. In any case, we reiterate our apologies and we would really appreciate that Reviewer#3 agrees to review the new version of the manuscript, whose quality is much higher. Thank you very much in advance.

Some detailed comments (typos/language issues are incomplete and formatting needs to be appropriate for a journal article)

L18 - A PID in English analytical literature is a Photoionization detector not a photo-metric ionization detector.

Thank you for spotting this error. This has been corrected in the manuscript.

L33-34 appropriate for a conclusion/outlook but not for an abstract.

This two lines have been removed. The new abstract is as follows: "*The European Union requires that benzene in air is continuously measured due to its toxicity and widespread presence in the population nuclei, mainly motivated by vehicle emissions. The reference measuring technique is gas chromatography (GC). Automatic chromatographs used in monitoring stations must verify the operating conditions established in Standard EN 14662 part 3, which includes a type approval section with a number of tests that analysers must pass. Among these tests, the potential interference of a number of compounds is evaluated. The 2005 version of the mentioned standard requires the evaluation of the potential interference of tetrachloromethane (TCM). The 2015 version eliminates TCM as a potential interferent. Although most consumer uses of TCM have been banned, recent studies have measured significant concentrations of TCM in air. In this paper, the potential interference of TCM on benzene measurements obtained with gas chromatography coupled to a photoionisation detector (PID) has been investigated. Our study shows that the simultaneous presence of benzene and TCM causes a significant decrease in benzene readings. For TCM concentrations of 0.7 µg m^{-3} (typical of urban areas) and 4.5 µg m^{-3} (detected in the vicinity of landfills), the relative errors in benzene measurements were 34 and 70 %, respectively, which are far too high compared to the maximum overall uncertainty allowed for benzene measurements (25 %). Possible mechanisms to qualitatively and quantitatively explain the behavior of the PID when measuring benzene with and without TCM have been proposed*".

L49 why is the degree underlined? Why is there random underlining of text and references?

Before it was sent to the reviewers, the editor handling the manuscript asked for making some changes in the manuscript. They were underlined to ease their locations in the text. All these underlines have now been removed.

L59 excess period

The excess period has been removed.

L61 and check rest of the manuscript it is “et al.” not “et. al” overall format references AND in text citations following author instructions.

References throughout the text have been managed with Mendeley and formatted to Copernicus citing style, so now there is consistency in all of them and follow the journal instructions.

L63 provide references/citations to the directive document

This reference has been added.

Table1: provide in the table (or table legend) where these values are form (reference?) as this is not from the present work.

Table 1 has been removed as it reported data that was not up to date and it was not relevant for the research.

L69 Statements like lifetime need to be supported by citations. Overall the whole introduction needs much more citations for the statements made (like L73 VOCs can affect human health.. based on what?).

Introduction section has been thoroughly revised. References have been added in all statements done. The two first paragraphs of the introduction are the following ones and can give an idea of the whole work done throughout the manuscript.

“*Benzene is a volatile organic compound (VOC) (Tisserand and Young, 2014). Directive 2008/50/EC (European Commission, 2008) defines them as organic compounds from anthropogenic and biogenic sources, other than methane, that are capable of producing photochemical oxidants by reactions with nitrogen oxides in the presence of sunlight. Benzene sources include natural emissions from vegetation and oceans (Misztal et al., 2015), microbial decomposition (Neves et al., 2005), wildfires (Wentworth et al., 2018) and volcanoes (Tassi et al., 2015); and anthropogenic emissions mainly from vehicles that use fossil fuels (von Schneidemesser et al., 2010) and, in central and northern European countries, from the combustion of wood used for domestic heating (Hellén et al., 2008). It is also present in tobacco smoke (Darrall et al., 1998) and in a wide range of industrial and household products (solvents, adhesives, paints and cleaning products), and is also a raw material for the synthesis of other products, such as dyes, detergents, plastics and explosives (Guenther et al., 1995). Its content in gasoline is regulated by Directive 2009/33/CE and it has to be < 1 % (v/v) (European Commission, 2009).*

Due to the chemical stability of benzene compared with most VOCs (with a half-life of 9.4 days (Atkinson, 2000)), its permanence in the atmosphere is high. Consequently, it can be transported over long distances. It is degraded by OH radicals in the troposphere, forming phenol and glyoxal, among other compounds (Atkinson, 2000; Volkamer et al., 2001). Benzene is a recognised inductor of leukaemia (D'Andrea and Reddy, 2016) and also affects the central nervous and immune systems and damages genetic material (Bahadar et al., 2014). Benzene is the only VOC whose concentrations in air are regulated in Europe. Its annual limit value is 5 µg m^{-3} at 293 K and 101.4 kPa and its monitorisation in air is mandatory (European Commission, 2008)".

L76 missing parenthesis.

This has been corrected.

L78 Why is there a section on introduction and background and objectives. There should only be an introduction. Overall the manuscript is not prepared using AMT instructions

These two sections have been merged into a single one and some of its content has been moved to other sections. The organisation of the paper has significantly changed and has adopted a typical structure of a scientific paper. AMT instructions for authors have been followed and a proper template has been used for the preparation of the revised version of the manuscript.

L81-83 and following: provide citations for standards

Citations for standards have been added:

CEN: EN 14662-1 Ambient air quality. Standard method for measurement of benzene concentrations. Pumped sampling followed by thermal desorption and gas chromatography, 2005a.

CEN: EN 14662-2 Ambient air quality. Standard method for measurement of benzene concentrations. Pumped sampling followed by solvent desorption and gas chromatography, 2005b.

CEN: EN 14662-3 Ambient air. Standard method for the measurement of benzene concentrations. Automated pumped sampling with in situ gas chromatography, 2005c.

CEN: EN 14662-3 Ambient air. Standard method for the measurement of benzene concentrations. Automated pumped sampling with in situ gas chromatography, 2015.

CEN: EN 14662-4 Ambient air quality. Standard method for measurement of benzene concentrations. Diffusive sampling followed by thermal desorption and gas chromatography, 2005d.

CEN: EN 14662-5 Ambient air quality. Standard method for measurement of benzene concentrations. Diffusive sampling followed by solvent desorption and gas chromatography, 2005e.

L150 please write chemical names correctly.. dimethylpentane (one word)

These names have been corrected. Thank you for spotting these mistakes.

L153 what is the electric density? Do you mean electron density?

We apologise for the mistake. These have been changed to *electric current*, which is the proper magnitude measured in the detector.

L185 it is typical in a scientific manuscripts to end the intro with 2-3 sentences of what is in the manuscript.

The new introduction section ends with the following lines: "*Given the above, in this paper, the potential interference of TCM on benzene measurements carried out by GC-PID is studied. A mechanism that explains the observed behaviour is also proposed*".

Experimental: info on source/ manufacturer purity of gases, purification material etc is critically missing.. please provide basic info on used reagents and used instrumentation including manufacturer location etc (see standard for the journal), Examples: L225 how were the concentrations obtained? Where are these gases from? Or L245 this is the only place where you give location etc as manufacturer info. This needs to be the case for everything, including the actual analyzers used!

Thank you for your comment. The experimental section has been revised and the maufacturers of equipment and reagents have been added. Also, the wording of the section has been changed and, hopefully, improved. As an example, the following is the first paragraph of the Experimental section:

"*An in-house designed controlled atmosphere chamber was used to generate dynamic test mixtures of benzene in air with and without TCM (Fig. 1). This chamber was used in previous works (Romero-Trigueros et al., 2016, 2017) and only a brief description will be given here. Zero air was generated from ambient air with a JUN-AIR compressor (Michigan, USA) provided with a drier, which is capable of reducing the relative humidity of the air down to 5 %. This dry air flows through three consecutive scrubbers containing silica gel (Merck, Darmstadt, Germany) and active charcoal (Chiemivall, Barcelona, Spain) to remove any traces of remaining humidity and other gases present in the air. After purification, a periodic check of organic pollutants in the zero air was carried out by gas chromatography, ensuring they were below their limits of detection. Benzene was incorporated to the zero air from a high-concentration gas mixture of benzene in nitrogen. Two mixtures of benzene in air from Abelló Linde (Valencia, Spain) were used at nominal amount fractions of 350 and 1000 µg m^{-3} (5 % expanded uncertainty). TCM was also incorporated from one of the two gas cylinders of TCM in nitrogen available in the laboratory (18 µg m^{-3} and 65 µg m^{-3}, 5 % expanded uncertainty) (Praxair, Guildford, UK) depending on the final concentrations required for our tests. All mixtures were certified by their respective manufacturers according to Standard ISO 6141:2000 (ISO, 2000). The flow rate of zero air and the target species were controlled and measured with Bronkhorst HI-TEC (Ruurlo, The Netherlands) mass flow controllers (ranges of 0–0.4 L min^{-1} for the benzene in nitrogen and TCM in nitrogen mixtures and 0–12 L min^{-1} for the zero air). The chamber allows for humidification of the mixtures with an in-house designed humidifier (Romero-Trigueros et al., 2017). Sample and environmental temperature can also be controlled as well as sample pressure at the inlet of the GC-PID. The laboratory was provided with a mercury barometer (Thies CLIMA, Göttingen, Germany), and high sensitivity Magnehelic gauges (Dwyer, Michigan, USA) were connected to the input of each chromatograph to maintain the flow at the reference pressure. Sample relative humidity and temperature were measured with a Testo 645 thermo hygrometer (Barcelona, Spain). All the tests carried out in the present work were done with dry gases at 20±2 ^{o}C and 1013 hPa*".

L254 why are bullet points used here? This is not common and not really warranted. Again this is a scientific manuscript not a report.

Bullet points have been removed from all over the paper.

Figure 5 seems to be used before figure 4. Make sure to use figures in the right order and number accordingly.

Figures have been renumbered according to their order of appearence in the text.

L325 what is the meaning of previous experiments. You show some of them here.. so this is not really previous? May be you men “initial”. Also if this is published already, you need full citation.

The *Experimental section* has been modified as well as the *Result and discussion* section. Now the *Experimental section* contains section *2.1. Experimental set-up,* and section *2.2. Experimental methods*. Inside the latter, section 2.2.1 describes the *experimental procedure to evaluate the potential interference of organic compounds according to Standard EN 14662:2005-3* (what was previously called “initial tests”). Section 2.2.2 describes the *experimental procedure to study the interference of TCM on benzene measurement*.

The *Result and discussion* section is organised following the two sub-sections of the *Experimental methods* section. Thus, inside section 3 *Results and discussion*, there is now two sub-sections: section 3.1 *Potential interference of organic compounds according to Standard EN 14662:2005-3*; and section 3.2. *Effect of TCM on benzene measurement*.

We the authors hope everything is clearer now.

L413 what is a magma? Did you mean “plasma” which would be the word for a partially ionized gas? Please use correct scientific language or explain what you mean? It is very uncommon to talk about a plasma (or magma) in the context of a PID.

We have to say that this is a clear “translation” error. We indeed mean the mixture with partially ionised gases. We have changed the word “magma” to “mixture”.

The following discussion is very weak as it is qualitative and not quantitative. What is a “strong electronegativity”? This has no real meaning.

We apologise for this. We shouldn’t have used electronegativity for a molecule as it is a property of bonded atoms. The correct magnitude is the electron affinity. A value of this parameter is also provided together with the reference from where it was obtained. The sentence has been changed to “*One part (pF) is directed towards the anode of the detector, and the other (qF) is retained by the TCM, given its relatively high electron affinity (2.2 eV) (Chen and Chen, 2004)*”.

L484-486 this not results and discussion but a statement that ends a conclusion

We have ended the Result and discussion section with the following paragraph (we think that a bit of a discussion and some guidelines to try to solve the issue are appropriate in this section):

"*As indicated in the standard EN 14662:2005-3, TCM was included as a possible interfering contaminant to be evaluated, but was not included in the 2015 version of the Standard. However, Sect. 8 of the current standard establishes that "some compounds, including carbon tetrachloride or butanol, may be present under site-specific conditions. In such cases, the responsibility for the proper determination of benzene falls on the network that operates the analyser by the appropriate choice of separation conditions (analytical column, temperature program of the column)". This approach would require continuous measurements of TCM in air and a knowledge of how TCM deviates measurements from its real value, which in turn, requires carrying out tests similar to those presented in this paper with dynamic dilution systems in controlled test atmospheres. This measure could not be easy to apply for economic and technical reasons so the whole responsibility must not only fall on the network managers. It seems reasonable that the manufacturers of the equipment tackle actions for solving this problem –or, at least, for reducing the extent of the interference in their measurements-, since they have the required technology and equipment. In any case, users of this type of equipment should be aware of the problem to try to minimise it. The discussion of this issue in the appropriate forum (e.g. the European Committee for Standardisation) seems also pivotal to reduce the uncertainty in benzene measurements by GC-PID in presence of TCM concentrations*".

Conclusions: This is not how conclusions are presented in a manuscript. For starters it is unusual to have numbered conclusions. Please write this like a conclusion in a scientific manuscript. In addition your first conclusion point 1. is not in this manuscript. This is not a conclusion of this manuscript

Conclusion section has been thoroughly modified. The new section is as follows:

"*The research described in this article has determined that TCM causes a significant interference in the measurement of benzene by GC-PID. This interference is negative, that is, readings of benzene are below their real ambient values, which may originates a mismanagement of the air quality of a location with presence of TCM in its air in relation to benzene.*

The relative error (RE) of the concentration of benzene measured as a function of the concentration of TCM (C_{TCM}) can be calculated from the following expression for the analyser tested in this work:

$$RE = (0.389.C_{TCM}^{0.388})\cdot 100$$

Thus, for C_{TCM} values of 0.7 µg m^{-3} (typical of urban areas) and 4.5 µg m^{-3} (in the vicinity of landfills), the REs in benzene measurements would be 34 and 70 %, respectively, independently of the concentration of benzene. These values are much higher than the overall expanded uncertainty allowed for benzene measurements with GC-PIDs. Given the importance of this interference, a possible mechanism has been proposed to explain the phenomenon when benzene is measured in the presence and absence of TCM. According to the proposed model, TCM attracts part of the electrons produced in the ionisation of benzene; thus, the electric current measured in the detector is lower than it should be. This interference is different in nature from that produced by other interfering species and, consequently, should be assessed independently of them.

Interestingly enough, it is established in part 3 of the standard EN 14662:2015 that the managers of the air quality monitoring network are responsible for determining the presence of TCM in the area where benzene is measured. If detected, they must act to eliminate the effect of the interferent. However, this approach would require continuous *measurements of TCM in air and a knowledge of how TCM deviates measurements from its real value, which in turn, requires carrying out tests similar to those presented in this paper with dynamic dilution systems in controlled test atmospheres. This may entail economic and technical issues so manufacturers of the chromatographs should try to solve this problem as they have greater technical and scientific capacity than network managers. In any case, all these issues should be discussed in the appropriate forum (e.g. the European Committee for Standardisation) in order to improve the uncertainty of benzene measurements and, thus, the management of the air quality*".

L517: Proofread your manuscript! Use a spell checker!!! Figure 1 quality is not acceptable: resolution, is too low Tables should be uniformly formatted English should be edited for better reading flow

Again, we are very sorry for the mistakes in the first version of the manuscript. We have proofread the new manuscript several times and have implemented all the changes suggested by the reviewers. Figure 1 has been removed as we have not been able to find it with better resolution. The information provided in Figure 1 has been described in the main text. Tables have been formatted according to AMT instructions. We hope the English style has also improved.

The interference of tetrachloromethane in the measurement of benzene in air by Gas Chromatography - Photoionisation Detector (GC-PID).

Authors: Cristina Romero-Trigueros[1], María Esther González*[2], Marta Doval Miñarro[3] and Enrique González[2]

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ABSTRACT

The European Union requires that benzene in air is continuously measured due to its toxicity and widespread presence in the population nuclei, mainly motivated by vehicle emissions. The reference measuring technique is gas chromatography (GC). Automatic chromatographs used in monitoring stations must verify the operating conditions established in Standard EN 14662 part 3, which includes a type approval section with a number of tests that analysers must pass. Among these tests, the potential interference of a number of compounds is evaluated. The 2005 version of the mentioned standard requires the evaluation of the potential interference of tetrachloromethane (TCM). The 2015 version eliminates TCM as a potential interferent. Although most consumer uses of TCM have been banned, recent studies have measured significant concentrations of TCM in air. In this paper, the potential interference of TCM on benzene measurements obtained with gas chromatography coupled to a photoionisation detector (PID) has been investigated. Our study shows that the simultaneous presence of benzene and TCM causes a significant decrease in benzene readings. For TCM concentrations of 0.7 µg m^{-3} (typical of urban areas) and 4.5 µg m^{-3} (detected in the vicinity of landfills), the relative errors in benzene measurements were 34 and 70 %, respectively, which are far too high compared to the maximum overall uncertainty allowed for benzene measurements (25 %). Possible mechanisms to qualitatively and quantitatively explain the behavior of the PID when measuring benzene with and without TCM have been proposed.

1. INTRODUCTION

Benzene is a volatile organic compound (VOC) (Tisserand and Young, 2014). Directive 2008/50/EC (European Commission, 2008) defines them as organic compounds from anthropogenic and biogenic sources, other than methane, that are capable of producing photochemical oxidants by

User1 Anon 25/1/19 15:33
Eliminado: iza

Usuario 5/2/19 16:18
Eliminado: [1]... Marta Doval Miñarro[32]...and ... [1]

Usuario 5/2/19 16:18
Eliminado: [1]

Usuario 5/2/19 16:18
Con formato: español

Usuario 5/2/19 16:18
Con formato: Inglés (británico)

Usuario 5/2/19 16:18
Eliminado: [2]

Usuario 15/1/19 13:14
Eliminado: the

User1 Anon 16/1/19 11:56
Eliminado: characteristics

Usuario 15/1/19 13:15
Eliminado: by

User1 Anon 23/1/19 12:29
Eliminado: For practical and safety reasons it is recommended that a photoionisationmetric ionisation detector (PID) is used.

Usuario 15/1/19 13:34
Eliminado: The ...a...tomatic chromatograp ... [2]

User1 Anon 16/1/19 11:57
Eliminado: was forbidden in ....have been banned

Usuario 15/1/19 13:31
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User1 Anon 28/1/19 10:17
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Usuario 15/1/19 13:31
Eliminado: ensure ...ave measured the ... [3]

User1 Anon 25/1/19 14:46
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User1 Anon 25/1/19 14:46
Con formato ... [4]

User1 Anon 25/1/19 14:45
Eliminado: µg/m^3

Usuario 15/1/19 13:36
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Usuario 15/1/19 13:37
Eliminado: unacceptable quality for the measurement of benzene...ar too high compared to the maximum overall uncertainty allowed for benzene measurements (25 %). Possible mechanisms have been proposed ...o qualitatively and quantitatively explain what happens in...he behavior of the PID when measuring benzene with and without benzene alone and in the prese ... [5]

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Usuario 17/1/19 12:49
Eliminado: ... [7]

reactions with nitrogen oxides in the presence of sunlight. Benzene sources include natural emissions from vegetation and oceans (Misztal et al., 2015), microbial decomposition (Neves et al., 2005), wildfires (Wentworth et al., 2018) and volcanoes (Tassi et al., 2015); and anthropogenic emissions mainly from vehicles that use fossil fuels (von Schneidemesser et al., 2010) and, in central and northern European countries, from the combustion of wood used for domestic heating (Hellén et al., 2008). It is also present in tobacco smoke (Darrall et al., 1998) and in a wide range of industrial and household products (solvents, adhesives, paints and cleaning products), and is also a raw material for the synthesis of other products, such as dyes, detergents, plastics and explosives (Guenther et al., 1995). Its content in gasoline is regulated by Directive 2009/33/CE and it has to be < 1 % (v/v) (European Commission, 2009).

Due to the chemical stability of benzene compared with most VOCs (with a half-life of 9.4 days (Atkinson, 2000)), its permanence in the atmosphere is high. Consequently, it can be transported over long distances. It is degraded by OH radicals in the troposphere, forming phenol and glyoxal, among other compounds (Atkinson, 2000; Volkamer et al., 2001).

Benzene is a recognised inductor of leukaemia (D'Andrea and Reddy, 2016) and also affects the central nervous and immune systems and damages genetic material (Bahadar et al., 2014). It is the only VOC in Europe whose concentrations in air are regulated. Its annual limit value is 5 $\mu g\ m^{-3}$ at 293 K and 101.4 kPa and its monitorisation in air is mandatory (European Commission, 2008). The standardised methods for the measurement of benzene concentrations in air were established by Directive 2008/50/EC (European Commission, 2008) and are described in the standard EN 14662 published in 2005, which is composed of five parts (CEN, 2005a, 2005b, 2005c, 2005d, 2005e). All parts are still valid, but part 3 was modified in 2015 (CEN, 2015). Each part describes a measuring method using gas chromatography (GC), but they differ in the sample collection and the automation of the analysis. Part 1 of the standard EN 14662 describes the sampling of air by pumping, using active carbon as an adsorbent and carrying out thermal desorption before the analysis. Part 2 differs from Part 1 in the desorption process, where carbon disulphide is used. Parts 4 and 5 describe a method where diffusive samplers are used to collect the sample, followed by thermal desorption (Part 4) or solvent desorption (part 5) and GC. Part 3 of the 2005 and 2015 versions of the standard describes an automated method of sampling and analysis, which is commonly used in air quality monitoring stations in Europe. Both versions contain a type approval section that consists of a series of tests that analysers must pass before commercialisation. Among the type approval tests, the potential interference of a number of substances has to be evaluated.

The 2005 version of the standard EN 14662-3 included a list of paraffinic, cyclic and halogenated organic compounds (including, tetrachloromethane (TCM)) that had to be tested as potential interferents. In the 2015 version, all hydrocarbons are maintained, isooctane (2,2,4-trimethylpentane) and 1-butanol have been added but TCM has been removed. Table 1 shows all the common and specific components of each version.

The synthesis of TCM for emissive uses was controlled and practically banned by the Montreal Protocol because it is an ozone-depleting substance (Sherry et al., 2018). However, its use as a raw material for the synthesis of other substances such as hydrofluorocarbons, pyrethroid pesticides or perchloroethylene is still allowed (Graziosi et al., 2016). Diffuse emissions may occur in its

User1 Anon 16/1/19 13:47
Eliminado: This group contains a diverse set of compounds with 15 carbon atoms or less, vapour pressures greater than 0.01 KPa at 20 ºC and boiling temperatures below 260 °C. Methane, organo-metallic compounds, carbon monoxide and carbon dioxide are excluded.... ... [8]

User1 Anon 16/1/19 12:02
Eliminado: ... [9]

User1 Anon 16/1/19 12:09
Eliminado: (with a half-life of 12 days)

Usuario 24/1/19 16:45
Eliminado: compared to other hydrocarbons of similar molecular mass

User1 Anon 16/1/19 23:00
Eliminado: and ...t is degraded by OH rad ... [10]

User1 Anon 16/1/19 12:11
Eliminado: ... [11]

User1 Anon 16/1/19 12:11
Eliminado: b...nzene is a recognised indu ... [13]

Usuario 5/2/19 17:20
Con formato ... [12]

Usuario 5/2/19 17:19
Eliminado: ... [14]

User1 Anon 28/1/19 20:08
Eliminado: in Europe in terms of air ... [15]

User1 Anon 25/1/19 14:47
Con formato: Superíndice

User1 Anon 16/1/19 12:11
Eliminado: (...nd its determination ...onit ... [16]

Usuario 24/1/19 9:38
Eliminado: (...ADDIN CSL_CITATION ... [17]

User1 Anon 28/1/19 20:08
Eliminado: ... [18]

Usuario 24/1/19 9:54
Eliminado: (EN, 2005a, b and c)... which i ... [19]

User1 Anon 16/1/19 12:13
Eliminado: the use... measuring method ... [20]

Usuario 24/1/19 9:46
Eliminado: aspiration

User1 Anon 16/1/19 12:16
Eliminado: in which...here carbon disulph ... [21]

User1 Anon 16/1/19 12:22
Bajado [1]: The Type Approval tests of th ... [22]

User1 Anon 16/1/19 12:26
Eliminado: <#>TCM exhibited differen ... [23]

User1 Anon 16/1/19 12:26
Eliminado: Figure 1. Benzene chromatog ... [24]

Usuario 24/1/19 9:57
Eliminado: (Sherry et al)

User1 Anon 16/1/19 12:37
Eliminado: a substance that destroys the ... [25]

Usuario 24/1/19 9:57
Eliminado: (Graziosi et al, 2016)

manufacture or during its use in the aforementioned syntheses. In this sense, 9500 MT of TCM were estimated to be emitted in 192 countries in 2007 (Penny et al., 2010). However, since the entry into force of the Montreal Protocol, there has been a progressive decrease in the environmental presence of TCM, with a decrease in its global average concentration of 10 to 15 pptv decade^{-1} (equivalent to 69 to 104 ng Nm^{-3} decade^{-1}) (Valeri et al., 2017). In 2005, the Agency for Toxic Substances and Disease Registry (ATSDR, 2005) determined a global average concentration of 0.7 µg Nm^{-3} with peaks in urban areas of 1.4 to 4.5 µg Nm^{-3} whereas 45 µg Nm^{-3} were detected in the vicinity of landfills (Brosas-Montecastro, 2008). More recent data collected in several cities of the world confirm average values of 0.61 µg Nm^{-3} in Lukang (Taiwan), 0.64 µg Nm^{-3} in Bristol (UK) and 1.10 µg Nm^{-3} in Bilbao (Spain) (de Blas et al., 2016). In this last city, maximum concentrations of 9.94 µg Nm^{-3} have been measured. These values justify the need for studying its potential interference on benzene measurements. It should also be noted that the global average lifetime of TCM reported in the recent literature is 44 years (36-58) (Ko et al., 2013; Valeri et al., 2017), so its effects, such as the one indicated here, will be manifested during the next decades.

Given the above, in this paper, the potential interference of TCM on benzene measurements carried out by gas chromatography coupled to photoionisation detector (GC-PID) is studied. A mechanism that explains the observed behaviour is also proposed.

2. Materials and methods

2.1. Experimental set-up

An in-house designed controlled atmosphere chamber was used to generate dynamic test mixtures of benzene in air with and without TCM (Fig. 1). This chamber was used in previous works (Romero-Trigueros et al., 2016, 2017) and only a brief description will be given here. Zero air was generated from ambient air with a JUN-AIR compressor (Michigan, USA) provided with a drier, which is capable of reducing the relative humidity of the air down to 5 %. This dry air flows through three consecutive scrubbers containing silica gel (Merck, Darmstadt, Germany) and active charcoal (Chiemivall, Barcelona, Spain) to remove any traces of remaining humidity and other gases present in the air. After purification, a periodic check of organic pollutants in the zero air was carried out by gas chromatography, ensuring they were below their limits of detection. Benzene was incorporated to the zero air from a high-concentration gas mixture of benzene in nitrogen. Two mixtures from Abelló Linde (Valencia, Spain) were purchased at nominal concentrations of 1000 and 350 µg m^{-3} of benzene (5 % expanded uncertainty). TCM was also incorporated from one of the two gas cylinders of TCM in nitrogen available in the laboratory (18 µg m^{-3} and 65 µg m^{-3}, 5 % expanded uncertainty) (Praxair, Guildford, UK) depending on the final concentrations required for our tests. All mixtures were certified by their respective manufacturers according to Standard ISO 6141:2000 (ISO, 2000). The flow rate of zero air and the target species were controlled and measured with Bronkhorst HI-TEC (Ruurlo, The Netherlands) mass flow controllers (ranges of 0–0.4 L min^{-1} for the benzene in nitrogen and TCM in nitrogen mixtures and 0–12 L min^{-1} for the zero air). The chamber allows for humidification of the mixtures with an in-house designed humidifier (Romero-Trigueros et al., 2017). Sample and environmental temperature can also be controlled as well as sample pressure at the inlet of the GC-PID. The laboratory was provided with a mercury barometer (Thies CLIMA, Göttingen, Germany), and high sensitivity Magnehelic gauges (Dwyer, Michigan, USA) were connected to the input of each chromatograph to maintain the flow at the reference pressure.

Usuario 24/1/19 10:04
Eliminado: Penny et al (2010) estimated ... [26]

User1 Anon 17/1/19 16:24
Eliminado: the...global average concentra ... [27]

User1 Anon 25/1/19 14:48
Eliminado: /

Usuario 24/1/19 10:06
Eliminado: (Valeri et al)... In 2005, the Ag ... [28]

User1 Anon 25/1/19 14:48
Con formato: Superíndice

User1 Anon 16/1/19 12:50
Eliminado: s...a global average concentra ... [29]

Usuario 24/1/19 10:15
Eliminado: Brosas (2008) detected

User1 Anon 25/1/19 14:48
Eliminado: /...m^{-33} ...were detected in the ... [30]

Usuario 24/1/19 10:25
Eliminado: provided by Blas et al. (2016)

User1 Anon 16/1/19 12:51
Eliminado: diverse...cities of the world c ... [31]

Usuario 24/1/19 10:26
Eliminado:

User1 Anon 17/1/19 17:16
Eliminado: from 26 to 35 years

Usuario 24/1/19 10:26
Eliminado: (SPARC, 2013;

User1 Anon 17/1/19 17:17
Eliminado: Liang et.al, 2014

Usuario 24/1/19 10:26
Eliminado: Valeri et al)

User1 Anon 17/1/19 17:03
Eliminado: two

User1 Anon 17/1/19 17:48
Eliminado: EXPERIMENTAL

User1 Anon 17/1/19 17:49
Eliminado: Test atmosphere: A standard atmosphere system

Usuario 24/1/19 10:28
Eliminado: (Romero-Trigueros, 2016; Romero-Trigueros, 2017)

User1 Anon 17/1/19 17:54
Movido (inserción) [2]

User1 Anon 17/1/19 18:02
Eliminado: the concentration levels of the organic pollutants in "zero" air were periodically checked... periodic check of organic polluta ... [32]

User1 Anon 25/1/19 14:49
Con formato ... [33]

Sample relative humidity and temperature were measured with a Testo 645 thermo hygrometer (Barcelona, Spain). All the tests carried out in the present work were done with dry gases at 293±2 K and 101.3 kPa.

The final concentration of component x (Cp_x, expressed in µg m^{-3}) after mixing all the gas flows can be determined from the mass balance expressed in Eq.(1).

$$Cp_x = Q_{bx} \cdot Cpb_x/(Q_a + \Sigma Q_b) \qquad \text{Eq. (1)}$$

where Cpb_x is the concentration of component x in the high concentration gas cylinder, Q_{bx} is the flow rate from the gas cylinder containing pollutant x, Q_a is the zero air flow rate and ΣQ_b is the sum of the rest of flow rates coming from gas cylinders. These concentrations and flow rates are expressed at 293 K and 101.3 KPa. These conditions were maintained at the entrance of each chromatograph for all tests. The expanded uncertainties of all generated concentrations of pollutants were estimated from the standard uncertainties of the high concentration gas cylinders and the standard uncertainties of the gas flow rates. In all cases, the final expanded uncertainty was less than 5 %, according to the limit established in Standard EN 14662-3.

Two identical type-approved BTEX Syntech Spectras GC955 chromatographs equipped with PIDs (Groningen, Netherlands) were tested in this work. These are widely used in European air pollution monitoring networks, and were identified as Analysers I and II, respectively. The analytical process is semi-continuous. While the GC-PID is analysing a sample, a new one is sampled and sent to the pre-concentration system. The air sampling system comprises a 35 mL capacity piston pump and the suction operation is repeated five times producing a total sample volume of 175 mL in each cycle. The successive 35 mL samples of air flow to a pre-concentrator (consisting of a column filled with Tenax), which retains the organic compounds and releases the excess air. Once the five suction cycles are completed, the contaminants retained in the pre-concentrator undergo thermal desorption and are carried with Nitrogen 5.0 towards the chromatographic column. The column was an AT-5 capillary column (15 m length x 0.32 mm diameter), and was composed of silica with a film of adsorbent polymer (1 µm heliflex coating) ideal for substances with boiling points between 40 and 250 °C. The initial oven temperature was set at 50 °C and maintained for 3 min, then increased to 70 °C at 10 °C min^{-1}. This temperature was maintained for 7 min before being reduced to 50 °C with a cooling rate of 10 °C min^{-1}. The windows used to quantify benzene in Analysers I and II were 176–212 s and 148–182 s, respectively. Each measurement cycle (from the first aspiration of air to the final result of the detected concentration) lasts for 15 min.

2.2. Experimental methods

2.2.1. Experimental procedure to evaluate the potential interference of organic compounds according to Standard EN 14662:2005-3

A first set of experiments was carried out according to Standard EN 14662:2005-3 with Analysers I and II for two different benzene nominal concentration (0.5 µg m^{-3} and 40 µg m^{-3}). The procedure consisted of generating a reference gas mixture of benzene in zero air with the desired

User1 Anon 18/1/19 10:58
Eliminado: which allowed "zero" air, and mixtures of air with benzene and/or TCM with known concentrations,...at a temperature ... [34]

User1 Anon 17/1/19 18:03
Eliminado: The airflows containing the components of interest (benzene and TCM) were prepared as in the installation shown in figure 2, which consisted of the following: ... [35]

User1 Anon 17/1/19 17:54
Subido [2]: After purification, the concentration levels of the organic pollutants in "zero" air were periodically checked by chromatographic analysis, ensuring they were below the limits of chromatographic detection.

User1 Anon 18/1/19 11:02
Eliminado: standard ...oncentration of po ... [36]

User1 Anon 25/1/19 14:50
Con formato: Superíndice

User1 Anon 18/1/19 11:03
Eliminado: µg/m³... after mixing all the ga ... [37]

User1 Anon 18/1/19 11:07
Eliminado: bottle of origin...igh concentra ... [38]

User1 Anon 18/1/19 11:11
Eliminado: ... [39]

User1 Anon 18/1/19 11:23
Bajado [3]: • To explain the behaviour of benzene in the PID, we proposed the model shown in figure 3, which also served as a basis to determine what happens in the presence of TCM (figure 5). When the gasified benzene (n, in molar units) leaves the column, pulled by the carrier gas, it accesses the PID where a fraction, F (≤1), is ionised by the radiation of the lamp, forming nF ionic couples (electrons and benzyl cations). This forms a magma that produces an electrical intensity when passing through the electrodes of the detector, whose area is proportional to the concentration of benzene in the sample, given that F is practically constant within the range of concentrations tested, as demonstrated by the experimental results. The benzyl ions recover the electrons in the cathode and benzene is reformed, hence the non-destructive nature of the detector.

User1 Anon 18/1/19 11:26
Eliminado: . ... [40]

User1 Anon 25/1/19 14:50
Con formato ... [41]

concentration, which was measured with the GC-PID. Afterwards, the organic compounds were added from an independent gas cylinder and the analyser measurements were compared with the previous ones. The effect of the dilution produced in the concentration of benzene in the reference gas mixture when adding the interferents was taken into account in the calculations. For each test, six individual measurements were taken to obtain statistically significant data, using the arithmetic mean as the representative value. A similar test was also carried out at a nominal concentration of benzene of 5 µg m^{-3} benzene in zero air, as this is the annual limit value of benzene concentrations in air in the EU (European Commission, 2008).

According to Standard EN 14662:2005-3, the parameters used to evaluate the deviations caused by the interferents are the effect of organic compounds (b_{Corg}, Eq. (2)), the standard uncertainty (U_{Corg}, Eq.(3)) and the test value (V_{test}, Eq.(4)). In these equations, C_{aCorg} is the average concentration of benzene in the presence of organic compounds measured by the analyser (µg m^{-3}) and C_a is the average concentration of benzene measured in the absence of organic compounds (µg m^{-3}). We have also used the relative error of the measurements to compare the results (Eq. (5)).

$$b_{Corg} = \left| C_{aCorg} - C_a \right| / C_a \quad \text{Eq. (2)}$$

$$U_{Corg} = \left| C_{aCorg} - C_a \right| / \sqrt{3} \quad \text{Eq. (3)}$$

$$V_{test.} = (U_{Corg} / C_a) \cdot 100 \quad \text{Eq. (4)}$$

$$RE = b_{Corg} \cdot 100 \quad \text{Eq. (5)}$$

In order to ensure that the biases obtained in these and subsequent experiments were only due to the interfering compounds tested, sample and surrounding temperature, sample pressure and voltage were kept constant during all experiments. A lack-of-fit test was performed in order to assess the accuracy of the readings. For this, after calibration of the analysers, several gas mixtures of benzene in air with different concentrations ranging from 0 to 50 µg m^{-3} were measured. Relative differences between the readings and the reference concentrations were calculated and, in all cases, were below 10%, much lower than the values reported in the Result and discussion Sect. due to the interference of TCM.

2.2.2. Experimental procedure to study the interference of TCM on benzene measurement

Due to the different nature of the interference of the organic compounds that reach the PID, separate studies should be carried out for those that positively (increasing) and negatively (decreasing) affect the measurements of benzene. As explained later, TCM causes the concentration of benzene to decrease, whereas the rest of them act positively; thus, independent tests studying only the influence of TCM were performed.

To study the effect of TCM on the GC-PID measurements of benzene, subsequent tests were performed with Analyser I. This decision was supported by the similar behaviour observed for both analysers when carrying out the tests described in Sect. 2.2.1. In addition, a reproducibility test was carried out in the lab. Both analysers were subject to measure simultaneously a gas mixture containing 5 µg m^{-3} nominal benzene in zero air. The reproducibility (in µg m^{-3}) was calculated as:

User1 Anon 18/1/19 12:33
Movido (inserción) [6]

User1 Anon 18/1/19 12:33
Eliminado: In…or each test, six individual ... [42]

User1 Anon 25/1/19 14:51
Con formato: Superíndice

Usuario 24/1/19 10:29
Eliminado: (DIrectiva)

User1 Anon 18/1/19 12:30
Movido (inserción) [5]

User1 Anon 18/1/19 12:32
Eliminado: These tests have been established in the earlier version of part 3 of the standard EN 14662, and involve comparing the responses of the chromatographs when analysing standards (C_p) containing benzene at two concentrations (one-tenth of the limit value established in the European legislation, Directive 2000/69/CE, and close to 70–90% of the maximum certification range) and mixtures of benzene and the organic compounds indicated in table 3, each with concentrations close to 10 µg/m^3.The measurements were obtained using the following sequence: ... [43]

User1 Anon 18/1/19 12:18
Movido (inserción) [4]

User1 Anon 18/1/19 12:20
Eliminado: where…C_{aCorg} is the average ... [44]

Usuario 5/2/19 17:21
Eliminado: difference

User1 Anon 18/1/19 12:21
Eliminado: ... [45]

Usuario 5/2/19 17:21
Con formato ... [46]

User1 Anon 18/1/19 12:18
Subido [4]: where C_{aCorg} is the average concentration of benzene chromatographic measurements in the presence of organic compounds (µg/m^3) and C_a is the average concentration of individual benzene measurements in the absence of organic compounds (µg/m^3)

User1 Anon 18/1/19 12:18
Eliminado: ... [47]

Usuario 24/1/19 16:42
Eliminado: t

User1 Anon 18/1/19 13:07
Movido (inserción) [7]

User1 Anon 18/1/19 13:07
Eliminado: chromatographic

$$Reproducibility = \sqrt{\frac{\sum d_i^2}{2n}}$$

where d_i is the i difference in readings between Analyser I and II and n is the total number of measurements (6 in our case). The value obtained was 0.067 µg m^{-3} when the average concentration of benzene in the reference gas mixture gas 4.6 µg m^{-3}, which means 1.5 % bias. This value was considered low enough to perform the subsequent tests with just one analyser.

Analyser I was first calibrated with dynamic reference gas mixtures of benzene (C_p) with nominal concentrations of 0, 2.5, 5, 10, 20 and 40 µg m^{-3}. Next, gas mixtures of benzene were prepared at the same concentrations but with the addition of TCM in nitrogen, such that the final concentrations of TCM (C_{TCM}) were 0.5, 1.0, 2.0 and 5.0 µg m^{-3}. The measurements of the latter mixtures produced the chromatographic reading C_{aTCM}. The TCM concentrations were selected due to its presence in urban areas at these levels (see Sect. 1). As before, Eq. 1 was used to calculate the flowrates of TCM and benzene in the different experiments. In all cases, each measurement was repeated six times.

3. Results and discussion

3.1. Potential interference of organic compounds according to Standard EN 14662:2005-3

The results obtained when carrying out the tests for evaluating the interference of organic compounds according to Standard EN 14662:2005-3 are shown in Table 2. Also, the results of a similar test with a nominal concentration of benzene of 5 µg m^{-3} are included. As can be seen in Table 2, the mixture of organic compounds interfered significantly, causing errors close to 60 % for the highest concentrations of benzene in the two chromatographs tested. When the reference concentration of benzene used was 5 µg m^{-3} significant negative deviations from this value were also observed in the presence of the mixture of organic compounds.

A similar result (Locoge et al., 2010) was obtained with the same GC-PID and a gas mixture of 5 µg m^{-3} benzene in air and 5 µg m^{-3} of each interfering substances in Table 1, according to EN 14662:2005-3. Benzene readings were 40 % lower than the expected value. The chromatographs obtained had 4 peaks. The first of them corresponded to 2-dimethylpentane, methylcyclopentane and 2,2,3-dimethylbutane; the second one to benzene, cyclohexane, 2-methylhexane and TCM; a third one to 3-ethylpentane; and a fourth one to n-heptane and trichloroethylene. Among the interferents of peak 2, only cyclohexane and 2-methylhexane increase the readings of benzene because their respective ionisation potentials (between 9.88 and 10.08 eV) are lower than the potential generated by the detector lamp (10.6 eV), and therefore the electric current in the detector increases, leading to an increase in the apparent concentration of benzene. However, TCM must exhibit a different behaviour as its ionisation potential (11.7 eV) is greater than that emitted by the lamp; therefore, it does not ionise and increase the intensity in the detector. It is evident that it acts inversely, since it significantly decreases the apparent benzene concentration. Further tests were carried out to study the nature and the extent of this interference (Sect. 3.2).

3.2. Effect of TCM on benzene measurement

Usuario 5/2/19 17:22
Eliminado: just

User1 Anon 18/1/19 13:28
Eliminado: the a...alysz...r I was first calib ... [48]

User1 Anon 18/1/19 13:17
Eliminado: ... [49]

User1 Anon 25/1/19 14:51
Con formato: Superíndice

User1 Anon 25/1/19 14:51
Con formato: Superíndice

User1 Anon 18/1/19 13:19
Eliminado: ,...leading to...roduced the ... [50]

User1 Anon 18/1/19 12:33
Eliminado: In each test, six individual measurements were made to obtain statistically significant data, using the arithmetic mean as a representative value (C_b)

User1 Anon 25/1/19 14:52
Con formato: Superíndice

User1 Anon 25/1/19 14:52
Con formato: Superíndice

User1 Anon 21/1/19 17:10
Con formato: No ajustar espacio entre texto latino y asiático, No ajustar espacio entre texto asiático y números

Usuario 24/1/19 10:29
Eliminado: by Locoge et al (2010)

User1 Anon 25/1/19 14:52
Con formato ... [51]

Usuario 24/1/19 11:17
Eliminado: the...ach interefering ... [52]

User1 Anon 18/1/19 14:06
Eliminado: **Previous experiments**
First, the organic interference tests were carried were carried out. These tests have been established in the earlier version of part 3 of the standard EN 14662, and involve comparing the responses of the chromatographs when analysing standards (C_p) containing benzene at two concentrations (one-tenth of the limit value established in the European legislation, Directive 2000/69/CE, and close to 70–90% of the maximum certification range) and mixtures of benzene and the organic compounds indicated in table 3, each with concentrations close to 10 µg/m^3. The results are shown in table 3 using the previously defined parameters. ... [53]

User1 Anon 16/1/19 12:22
Movido (inserción) [1] ... [54]

User1 Anon 18/1/19 13:35
Eliminado: First, the organic interference tests were carried out. These tests have been established in the earlier version of part 3 of the standard EN 14662, and involve comparing the responses of the chromatographs when analysing standards (... [55]

User1 Anon 18/1/19 12:30
Subido [5]: These tests have been established in the earlier version of part 3 of the standard ... [56]

User1 Anon 18/1/19 12:59
Eliminado: Due to the different behaviours of organic compounds that reach the PID in th ... [57]

Table 3 gathers the results of the tests performed according to Sect. 2.2.2. It can be seen that the presence of TCM significantly decreases the readings of benzene with respect to the reference gas mixture concentrations (C_p). Moreover, the deviations increase with increasing TCM concentrations. Otherwise, for the same TCM concentration, the relative difference of the readings for increasing benzene concentrations remained practically constant. The minimum average deviation found was 27.3 % (2.74 SD) for TCM concentrations of 0.5 µg m^{-3}. The maximum average deviation found was 68.5 % (2.78 SD) for TCM concentration of 5 µg m^{-3}.

The experimental values of C_a and C_{aTCM} were plotted versus C_p (Fig. 2 and Fig. 3). Linear relationships between C_a or C_{aTCM} and C_p were found for each series (p<0.001). All lines passed through the origin of coordinates, leading to the general equations Eq.(6) and Eq. (7):

$$C_a = K^* C_p \text{ (without TCM) Eq. (6)}$$

$$C_{aTCM} = K C_p \text{ (with TCM) Eq. (7)}$$

where K* and K are the slopes of the respective straight lines. These slopes decrease with increasing TCM concentrations. Table 4 shows Eqs. (6) and (7) with the value of the parameter K* or K obtained experimentally for each conducted test. A decrease in K was observed as the concentration of the interferent increased.

An analysis of the analytical method was done in order to understand the nature of this interference. For a substance to act as an interfering agent, it must have a retention time in the chromatographic column within the interval of identification of benzene, so that both species reach the detector within this interval. If this applies, the interference causes an increase or decrease in the detector signal. When the chromatograph has a PID, one of the following can occur: (i) If any organic compound other than benzene is ionised by the radiation of the detector lamp, the electric current increases, which leads to an increase in the readings of benzene. For this to happen, the ionisation potential of the interferent must be lower than that associated with the radiation of the lamp; or (ii) the interferent causes a decrease in the benzene signal, which can be due to several reasons. One of them is that the radiation of the detector lamp is absorbed to a greater or lesser extent by the interferent, and the remaining energy is insufficient to completely ionise the benzene. This phenomenon is known as "quenching effect" (Chou, 1999). This is the nature of the interference of humidity on benzene measurements (Romero-Trigueros et al., 2017). The second reason is that the interferent absorbs (blocks) part of the formed ions that participate in the quantification of benzene, leading to a decrease in the detected concentration. This mechanism is known as quenching effect via electron capture (Senum, 1981). As discussed below, TCM acts in this way.

To explain the behaviour of benzene in the PID, we have proposed the model shown in Fig. 4, which also serves as a basis to determine what happens in the presence of TCM, Fig. 5. When the gasified benzene (n, in molar units) leaves the column, dragged by the carrier gas, it accesses the PID where a fraction, F (≤1), is ionised by the radiation of the lamp, forming nF ionic couples (electrons and benzyl cations). This forms a mixture that produces an electric current when passing through the electrodes of the detector, which is shown as a peak, whose area is proportional to the concentration of benzene in the sample, given that F is practically constant within the range of

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Subido [7]: To study the effect of TCM on the chromatographic measurements of benzene, the analyzer was first calibrated (C_a versus C_p) to standard concentrations (C_p) of the pollutant, approximately 0, 2.5, 5, 10, 20 and 40 µg/m^3.

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concentrations tested, as demonstrated by the experimental results. The benzyl ions recover the electrons in the cathode and benzene is reformed, hence the non-destructive nature of the detector.

When an air sample, containing benzene (n moles) and TCM (m moles), accesses the PID, the lamp ionises a fraction F of benzene but does not act on the TCM, since its ionisation potential is greater than that provided by the lamp. When the ionic mixture is formed, the mechanisms that take place are complex, given that the electrons formed by the benzene ionisation (nF) are distributed between two competing paths. One part (pF) is directed towards the anode of the detector, and the other (qF) is retained by the TCM, given its relatively high electron affinity (2.2 eV) (Chen and Chen, 2004). Thus, the measurement in the detector (pF) depends on the electric fields configured by both systems and the relative amounts of benzene (n) and TCM (m). This may cause one of the species to be limiting, which also affects the final distribution. Eventually, the system evolves as shown in Fig. 5, the electric circuit closes and the initial species are regenerated.

According to Fig. 4, the concentration of benzene read by the chromatograph in the absence of TCM (C_a) can be expressed by means of Eq. (8).

$$C_a = C_p = n.F.M_b / V_T = n.F.\alpha_b \qquad \text{Eq. (8)}$$

where M_b is the molecular mass of benzene, V_T is the volume of the air sample and $\alpha_b = M_b/V_T$. When benzene and TCM simultaneously coexist, the measurements of benzene (C_{aTCM}) for a given concentration of TCM follow the generic representation in Fig. 5. Equation (9) was deduced from our experiments (Fig. 3).

$$C_{aTCM} = K.C_p = C_p - \Delta \qquad \text{Eq. (9)}$$

where Δ is the deviation of C_{aTCM} from C_p.

As can be deduced from Fig. 2 and Fig. 3, Δ was proportional to C_p for each C_{TCM}, and was also dependent on C_{TCM}. Based on the above, the following function was proposed:

$$\Delta = C_p.\ \varphi(C_{TCM}) \qquad \text{Eq. (10)}$$

Thus, based on Fig. (3) and Fig. (5) and Eqs. (9) and (10), C_{aTCM} can be expressed as follows.

$$C_{aTCM} = p.F.\alpha_b = (n - q).F.\alpha_b = C_p - q.F.\alpha_b = C_p - \Delta = C_p - C_p.\varphi(C_{TCM}) = [1 - \varphi(C_{TCM})].C_p \qquad \text{Eq. (11)}$$

From Eqs. (9) and (11):

$$1 - K = \varphi(C_{CTM}) \qquad \text{Eq. (12)}$$

Table 4 shows the values of 1 – K for each TCM concentration tested. The best fit is represented by the following equation:

$$1 - K = 0.389.C_{TCM}^{\ 0.388} \quad (r^2 = 0.988) \qquad \text{Eq. (13)}$$

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Figure 5. Simplified model of the behaviour of behaviour of benzene and TCM when interacting simultaneously in the PID detector ... [67]

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From Eqs. (9), (11) and (13):

$$C_{aTCM} = (1 - 0.389.C_{TCM}^{0.388})\, C_p \quad \text{Eq. (14)}$$

With Eq. (15), the relative error (RE) of benzene measurements by GC-PID in the presence of TCM can be estimated for Analyser I:

$$RE = [(C_{aTCM} - C_p)/C_p].100 = (0.389.C_{TCM}^{\ 0.388}).100 \qquad \text{Eq. (15)}$$

Thus, for TCM concentrations of 0.7, 1.4 and 4.5 µg m^{-3} (levels that are currently found in urban areas), biases in benzene readings close to 34, 44 and 70 %, respectively, may occur. These deviations are high and not acceptable if compared to the overall expanded uncertainty allowed in the legislation for benzene measurements (25 %).

As indicated in the standard EN 14662:2005-3, TCM was included as a possible interfering contaminant to be evaluated, but it was not included in the 2015 version of the Standard. However, Sect. 8 of the current standard establishes that *"some compounds, including carbon tetrachloride or butanol, may be present under site-specific conditions. In such cases, the responsibility for the proper determination of benzene falls on the network that operates the analyser by the appropriate choice of separation conditions (analytical column, temperature program of the column)"*. However, technicians that operate air quality networks usually lack of knowledge and tools to choose the optimum conditions for the analysis. On the other hand, a correction of readings would require continuous measurements of TCM in air and a knowledge of how TCM deviates measurements from its real value, which in turn, requires carrying out tests similar to those presented in this paper with dynamic dilution systems in controlled test atmospheres. This measure could not be easy to apply for economic and technical reasons so the whole responsibility must not only fall on the network managers. It seems reasonable that the manufacturers of the equipment tackle actions for solving this problem –or, at least, for reducing the extent of the interference in their measurements-, since they have the required technology and equipment. In any case, users of this type of equipment should be aware of the problem to try to minimise it. The discussion of this issue in the appropriate forum (e.g. the European Committee for Standardisation) seems also pivotal to reduce the uncertainty in benzene measurements by GC-PID in presence of TCM concentrations.

CONCLUSIONS

The research described in this article has determined that TCM causes a significant interference in the measurement of benzene by GC-PID. This interference is negative, that is, readings of benzene are below their real ambient values, which may originates a mismanagement of the air quality of a location with presence of TCM in its air in relation to benzene.

The relative error (RE) of the concentration of benzene measured as a function of the concentration of TCM (C_{TCM}) has been obtained for Analyser I and, presumably, other GC-PIDs will follow similar

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expressions. Thus, for C_{TCM} values of 0.7 μg m^{-3} (typical of urban areas) and 4.5 μg m^{-3} (in the vicinity of landfills), the REs in benzene measurements would be 34 and 70 %, respectively, independently of the concentration of benzene. These values are much higher than the overall expanded uncertainty allowed for benzene measurements with GC-PIDs. Given the importance of this interference, a possible mechanism has been proposed to explain the phenomenon when benzene is measured in the presence and absence of TCM. According to the proposed model, TCM attracts part of the electrons produced in the ionisation of benzene; thus, the electric current measured in the detector is lower than it should be. This interference is different in nature from that produced by other interfering species and, consequently, should be assessed independently of them.

Interestingly enough, it is established in part 3 of the standard EN 14662:2015 that the managers of the air quality monitoring network are responsible for determining the presence of TCM in the area where benzene is measured. If detected, they must act to eliminate the effect of the interferent. However, this approach would require continuous measurements of TCM in air and a knowledge of how TCM deviates measurements from its real value, which in turn, requires carrying out tests similar to those presented in this paper with dynamic dilution systems in controlled test atmospheres. This may entail economic and technical issues so manufacturers of the chromatographs should try to solve this problem as they have greater technical and scientific capacity than network managers. In any case, all these issues should be discussed in the appropriate forum (e.g. the European Committee for Standardisation) in order to improve the uncertainty of benzene measurements and, thus, the management of the air quality.

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CEN: EN 14662-2 Ambient air quality. Standard method for measurement of benzene concentrations. Pumped sampling followed by solvent desorption and gas chromatography, 2005b.

CEN: EN 14662-3 Ambient air. Standard method for the measurement of benzene concentrations. Automated pumped sampling with in situ gas chromatography, 2005c.

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4. Of note

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Tables

Table 1. Organic compounds used to assess interferences in the measurement of benzene in air, in accordance with standards EN 14662-3 (2005 and 2015 versions).

<table>
<tr><th>EN 14662-3:2005</th><th>EN 14662-3:2015</th></tr>
<tr><td colspan="2">Methylcyclopentane</td></tr>
<tr><td colspan="2">2,2,3- Trimethylbutane</td></tr>
<tr><td colspan="2">2,4-Dimethylpentane</td></tr>
<tr><td colspan="2">Cyclohexane</td></tr>
<tr><td colspan="2">2,3-Dimethylpentane</td></tr>
<tr><td colspan="2">2-Methylhexane</td></tr>
<tr><td colspan="2">3-Ethylpentane</td></tr>
<tr><td colspan="2">Trichlorethylene</td></tr>
<tr><td colspan="2">n-Heptane</td></tr>
<tr><td>Tetrachloromethane</td><td>1-Butanol</td></tr>
<tr><td></td><td>2,2,4-Trimethylpentane</td></tr>
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Percentage (%) ... [83]

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Table 2. Results obtained when conducting the test to evaluate the interference of organic compounds in benzene readings for Analysers I and II. Nominal concentrations tested: 0.5 and 40 µg m^{-3} (according to Standard EN 14662:2005-3) and 5 µg m^{-3}. Standard deviation of 6 measurements shown in parenthesis.

Concentration of reference gas mixture: C_p C_6H_6 (µg m^{-3})	Concentration of reference gas mixture: C_p organic compounds (µg m^{-3})	Analyser readings (µg m^{-3})	RE (%)	U_{Corg} (µg m^{-3})	V_{test} (%)
ANALYSER I					
0.50	0.00	C_a: 0.48 (0.04)			
0.00	10.00	0.05 (0.00)	2.25	0.01	1.30
0.50	10.00	C_{aCorg}: 0.49 (0.04)			
32.55	0.00	C_a: 33.07 (0.25)			
0.00	10.00	0.05 (0.00)	60.7	11.6	35.1
32.55	10.00	C_{aCorg}: 13.00 (1.05)			
4.68	0.00	C_a: 4.64 (0.02)			
0.00	10.00	0.05 (0.00)	69.2	1.85	39.9
4.68	10.00	C_{aCorg}: 1.43 (0.08)			
ANALYSER II					
0.50	0.00	C_a: 0.48 (0.04)			
0.00	10.00	0.05 (0.00)	3.37	0.01	1.95
0.50	10.00	C_{aCorg}: 0.50 (0.03)			
39.50	0.00	C_a: 39.58 (0.25)			
0.00	10.00	0.05 (0.00)	60.6	13.8	35.0
39.50	10.00	C_{aCorg}: 15.61 (0.36)			
5.06	0.00	C_a: 5.03 (0.17)			
0.00	10.00	0.05 (0.00)	40.4	1.17	23.3
5.06	10.00	C_{aCorg}:3.00 (0.01)			

Table 3. Average readings of benzene obtained with Analyser I when measuring benzene reference gas mixtures without TCM (C_a) and with TCM (C_{aTCM}). Standard deviation of 6 measurements shown in parenthesis.

Series I: C_{TCM} = 0.5 µg m^{-3}			
C_p C_6H_6 (µg m^{-3})	C_a (without TCM) (µg m^{-3})	C_{aTCM} (with 0.5 µg m^{-3} de TCM) (µg m^{-3})	RE (%)
0.00	0.00 (0.00)	-0.01 (0.00)	-
1.15	1.17 (0.01)	0.90 (0.05)	22.90
3.48	3.45 (0.03)	2.43 (0.01)	29.56
8.62	8.55 (0.15)	6.10 (0.14)	28.61
22.25	20.19 (0.12)	14.32 (0.12)	29.07

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User1 Anon 25/1/19 14:46
Eliminado: µg/m[3]
Usuario 5/2/19 16:14
Con formato ... [87]
Usuario 24/1/19 15:30
Eliminado: what is established in part 3 of the s
Usuario 5/2/19 16:14
Con formato ... [88]
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Eliminado: z
User1 Anon 21/1/19 18:47
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Usuario 24/1/19 15:35
Eliminado: C_b
User1 Anon 25/1/19 10:06
Tabla con formato ... [91]
User1 Anon 25/1/19 14:54
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Eliminado: /...[-33] ... [90]
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User1 Anon 6/2/19 12:19
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... [103]

C_p C_6H_6 ($\mu g\ m^{-3}$)	C_a (without TCM) ($\mu g\ m^{-3}$)	C_{aTCM} (with 0.5 $\mu g\ m^{-3}$ de TCM) ($\mu g\ m^{-3}$)	RE(%)
42.60	42.57 (0.28)	31.32 (0.16)	26.42
Series II: C_{TCM} = 1.0 $\mu g\ m^{-3}$			
C_p C_6H_6 ($\mu g\ m^{-3}$)	C_a (without TCM) ($\mu g\ m^{-3}$)	C_{aTCM} (with 0.5 $\mu g\ m^{-3}$ de TCM) ($\mu g\ m^{-3}$)	RE(%)
0.00	0.00 (0.00)	-0.01 (0.00)	-
1.25	1.21(0.01)	0.72 (0.00)	40.33
3.55	3.45 (0.02)	2.03 (0.03)	41.16
8.70	8.49 (0.09)	5.01 (0.06)	40.99
20.31	20.22 (0.13)	11.88 (0.05)	41.25
42.89	43.01 (0.19)	25.68 (0.07)	40.29
Series III: C_{TCM} = 2.0 $\mu g\ m^{-3}$			
C_p C_6H_6 ($\mu g\ m^{-3}$)	C_a (without TCM) ($\mu g\ m^{-3}$)	C_{aTCM} (with 0.5 $\mu g\ m^{-3}$ de TCM) ($\mu g\ m^{-3}$)	RE(%)
0.00	0.00 (0.00)	-0.01 (0.00)	-
2.49	2.26 (0.01)	1.00 (0.01)	55.75
5.00	5.07 (0.02)	2.18 (0.03)	57.00
11.32	11.40 (0.11)	4.64 (0.04)	59.30
23.77	23.85 (0.11)	10.19 (0.24)	57.27
42.49	42.57 (0.28)	20.95 (0.10)	50.79
Series IV: C_{TCM} = 5.0 $\mu g\ m^{-3}$			
C_p C_6H_6 ($\mu g\ m^{-3}$)	C_a (without TCM) ($\mu g\ m^{-3}$)	C_{aTCM} (with 0.5 $\mu g\ m^{-3}$ de TCM) ($\mu g\ m^{-3}$)	RE(%)
0.00	0.00 (0.00)	-0.01 (0.00)	-
3.35	3.41 (0.2)	1.18 (0.01)	65.40
5.56	5.73 (0.03)	1.97 (0.02)	65.62
10.01	9.86 (0.10)	2.88 (0.05)	70.79
20.04	19.80 (0.14)	5.88 (0.10)	70.30
40.02	40.42 (0.18)	11.87 (0.09)	70.63

Table 4. Calibration lines of Analyser I obtained by linear regression (without TCM (C_a) and with TCM (C_{aTCM})). R^2 is shown in brackets. Parameter (1-K) is also shown.

Series	C_{TCM} ($\mu g\ m^{-3}$)	Calibration $C_a = K^* C_p$ (R^2)	$C_{aTCM} = K\ C_p$ (R^2)	1-K
I	0.00	$C_a = 0.980\ C_p$ (0.997)	---	---
	0.50	---	$C_{aTCM} = 0.715\ C_p$ (0.995)	0.285
II	0.00	$C_a = 1.00\ C_p$ (0.999)	---	---
	1.00	---	$C_{aTCM} = 0.595\ C_p$ (1.00)	0.405
III	0.00	$C_a = 1.00\ C_p$ (1.00)	---	---
	2.00	---	$C_{aTCM} = 0.474\ C_p$ (0.992)	0.526

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IV	0.00	$C_a = 1.01\ C_p$	(1.00)	---		---
	5.00	---		$C_{aTCM} = 0.297\ C_p$	(0.998)	0.703

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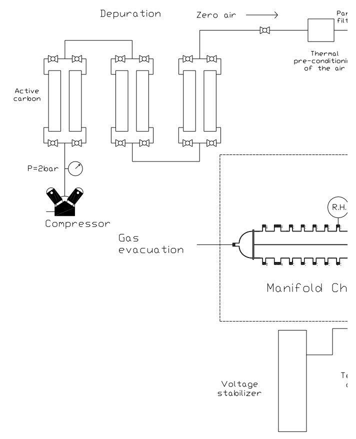

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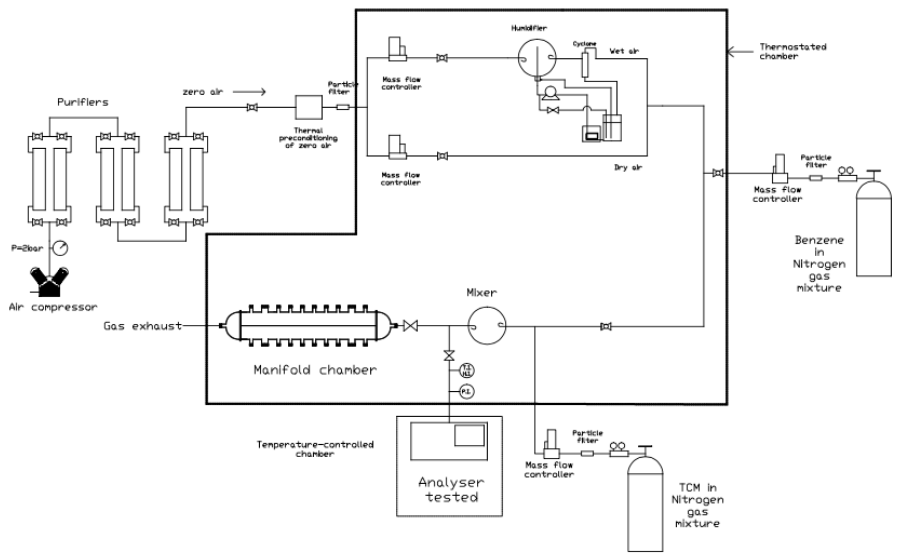

Figure 1: Schematic of the components of the controlled atmosphere chamber used to obtain gas mixtures of benzene in air with and without potential interferent substances. (HI: Humidity indicator, TI: Temperature indicator, PI: Pressure indicator)

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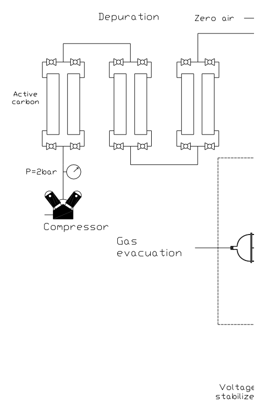

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Eliminado: Figure 21. Diagram Schematic of the components of the standard controlled atmosphere installation used to obtain air flows with benzene and/or TCM at known concentrations.generate reference gas mixtures of benzene and/or TCM.

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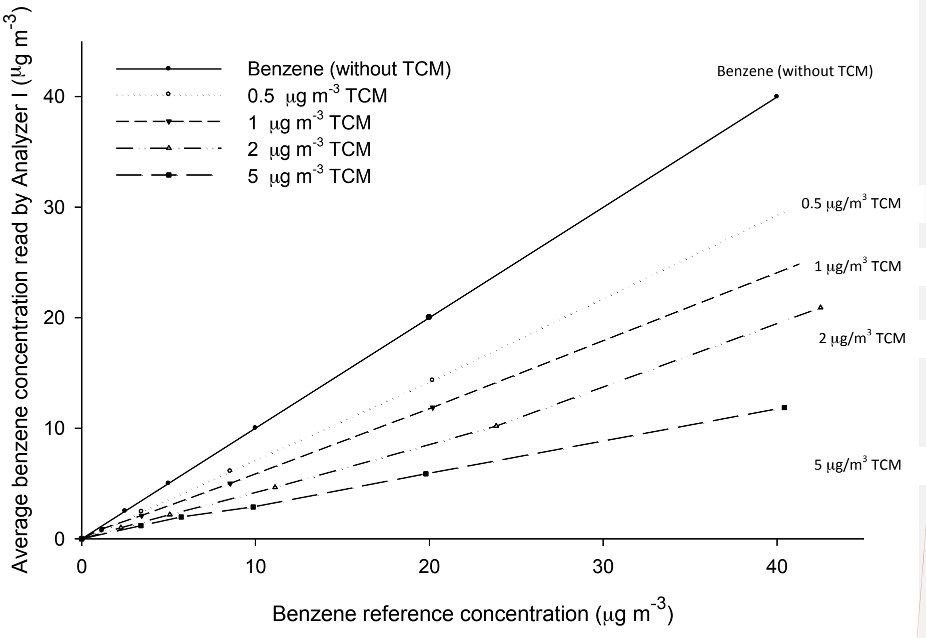

Figure 2: Calibration lines for Analyser I with and without TCM at different concentration levels.

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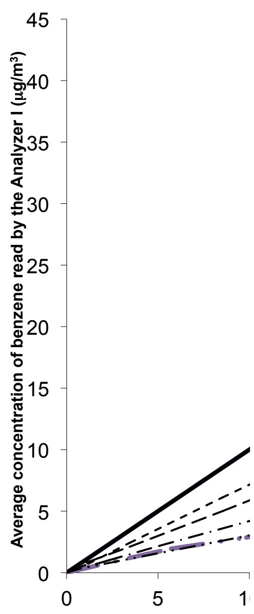

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Comentario [1]: Esta figura y la siguente hay que cambiarlas porque la figura tiene que ser un todo, no vale ponerle etiquetas con las concentraciones de cada curva encima del gráfico (como está ahora). Además hay que cambiar la forma de poner las unidades de la concentración a µg m-3

Si puedes, pídele a Esther los archivos originales. Tampoco entiendo por qué hay una línea morada (la de 5 ug/m3)

User1 Anon 6/2/19 15:12

Eliminado: Figure 3. Calibration lines of Analyser I for benzene with and without TCM at different concentrations.

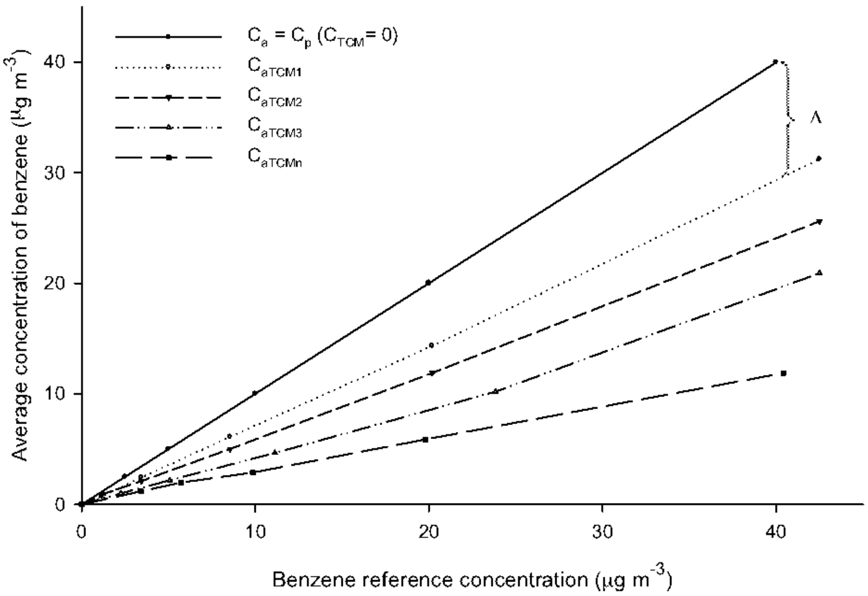

Figure 3: A generic representation of benzene readings as a function of the concentration of benzene and TCM in the reference gas mixture.

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Eliminado: Figure 4. Generic representations of benzene readings by a chromatograph (C_a and C_{aTCM}) *versus* reference concentrations (C_p).

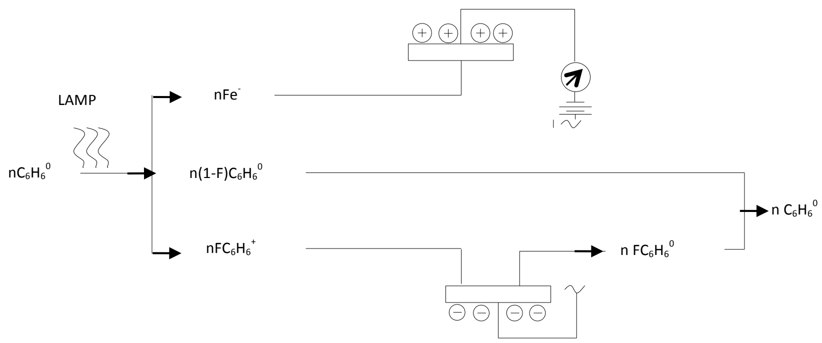

Figure 4. Schematic of the behaviour of benzene in the PID of the chromatograph in absence of TCM.

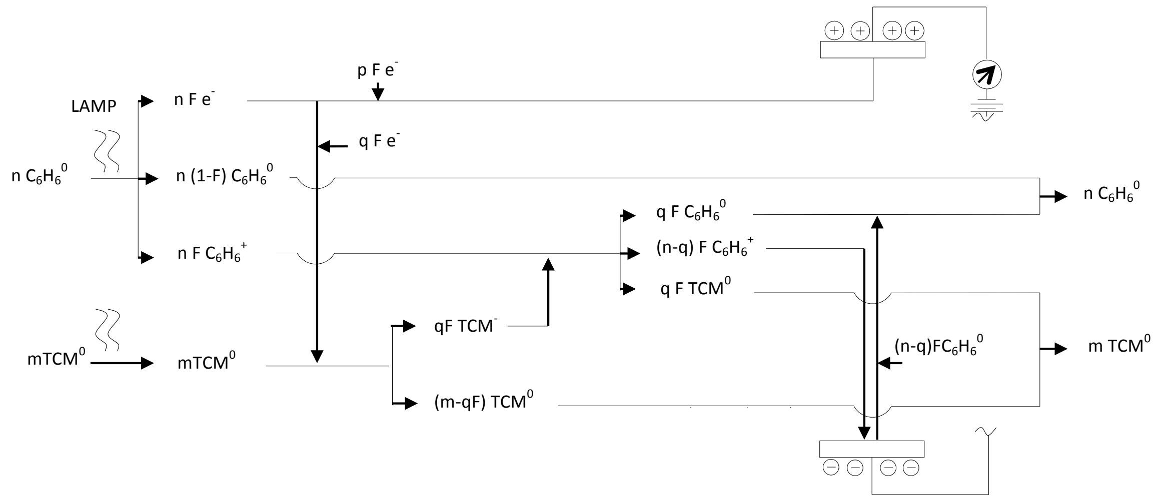

Figure 5: Schematic of the behaviour of benzene and TCM when they interact simultaneously in the PID detector.

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Eliminado: Figure 5. Simplified model of the behavior of benzene and TCM when they interact simultaneously in the PID detector.
Salto de sección (Página siguiente)