1 The interference of tetrachloromethane in the measurement of benzene in air by Gas
2 Chromatography - Photoionization Detector (GC-PID).
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12
13 **ABSTRACT**
14
15 The European Union requires that the benzene in air is measured due to its toxic characteristics and
16 widespread presence in the population nuclei, motivated by vehicle emissions. The reference
17 measuring technique is by gas chromatography (GC). For practical and safety reasons it is
18 recommended that a photometric ionisation detector (PID) is used. The automatic chromatographs
19 used in the monitoring stations must verify the operating conditions in the standard EN 14662:2005
20 part 3, which describes the Type Approval Tests. One of the tests determines possible
21 interferences, including by tetrachloromethane (TCM). Part 3 of the cited standard was modified in
22 2015, eliminating TCM as a possible interferer. Given that some studies ensure the presence of said
23 product in air, there has been considerable interest in testing different mixtures of benzene and
24 TCM.
25
26 This study has shown that the simultaneous presence of benzene and TCM causes a significant
27 decrease in the first GC-PID readings. For TCM concentrations of 0.7 $\mu g/m^3$ (typical of urban areas)
28 and 4.5 $\mu g/m^3$ (detected in the vicinity of landfills), the relative errors in benzene concentration
29 were 34 and 70%, respectively, which are of unacceptable quality for the measurement of benzene.
30 Possible mechanisms have been proposed to qualitatively and quantitatively explain what happens
31 in the PID with benzene alone and in the presence of TCM.
32
33 Given the significant impact of the interferer, it is important to open a discussion forum to address
34 this issue.
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46 **INTRODUCTION**
47
48 Benzene is a volatile organic compound (VOC). This group contains a diverse set of compounds with
49 15 carbon atoms or less, vapour pressures greater than 0.01 KPa at 20 ºC and boiling temperatures
50 below 260 $^{\circ}$C. Methane, organo-metallic compounds, carbon monoxide and carbon dioxide are
51 excluded.
52
53 Benzene originates from natural emissions (from vegetation, oceans, soils, sediments, microbial
54 decompositions and volcanoes) and anthropogenic emissions from fossil fuels (mainly from vehicles
55 and to a lesser extent from the combustion of wood that is widely used in central and northern
56 European countries for domestic heating). It is also present in tobacco smoke and in a wide range of
57 industrial and household products (solvents, adhesives, paints and cleaning products), and is also a
58 raw material for the synthesis of other products, such as dyes, detergents, plastics and explosives
59 (Guenther et al.1995). .
60
61 In Europe, the greatest anthropogenic emission of benzene is from vehicles (Sarigiannis et.al 2011),
62 with a contribution estimated at 80–85%, as shown in table 1. Currently, its presence is regulated in
63 petroleum automotives by Directive 2009/33/CE, and there must be less than 1% by volume
64 emitted.
65
66 Table 1. Contribution of the main anthropogenic sources of benzene in Europe.
67
68 Due to the chemical stability of benzene compared with most VOCs, its permanence in the
69 atmosphere is high (with a half-life of 12 days) compared to other hydrocarbons of similar
70 molecular mass. Consequently, it can be transported over long distances and degraded by OH
71 radicals in the troposphere, forming phenol and glyoxal, among other compounds.
72
73 VOCs can affect human health, and benzene is a recognised inductor of leukaemia and also affects
74 the central nervous system, deteriorates the immune system and damages genetic material.
75 Benzene is the only VOC regulated in Europe in terms of air quality; the annual average limit is 5
76 µg/m^3 (and its determination in air is mandatory, especially in urban centers.
77
78 **BACKGROUND AND OBJECTIVES**
79
80 The standardised methods in Europe for the measurement of benzene concentrations in air have
81 been established by Directive 2008/50/EC and are described in the standard EN 14662 published in
82 2005, which is composed of three parts. The first two parts are still valid, but part 3 was modified in
83 2015. Each part describes the use of GC with a capillary column, but they differ in methods of
84 sample collection and analytical automation. Part 1 of the standard EN 14662 describes the
85 sampling of air by aspiration, using active carbon as an adsorbent and carrying out thermal
86 desorption before the analysis. Part 2 differs in the desorption process, in which carbon sulphide is
87 used. Carbon sulphide was the most widely used solvent for VOCs captured on carbonaceous
88 adsorbents in industrial hygiene and atmospheric pollution testing. Currently, carbon sulphide is
89 not used.

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91 Part 3 of the 2005 and 2015 versions of the standard describes a method based on ambient air
92 sampling and automatic analysis, which is commonly used in measuring stations for atmospheric air
93 pollution in Europe. Both versions describe Type Approval that consists of a series of tests that are
94 carried out in accredited laboratories. In Europe, it is mandatory that air pollutant measuring
95 equipment complies with the aforementioned requirements before commercialisation.

96

97 The Type Approval tests of the two versions (2005 and 2015) of the cited standards and other
98 complementary tests were carried out in our laboratory under controlled conditions. Two articles
99 have been previously published regarding the effect of absolute air pressure at the entrance of the
100 chromatographs (Romero et al.2016), humidity and ambient temperature on the benzene
101 measurements (Romero et al.2017).

102

103 This article describes the possible interference of organic compounds that coexist in ambient air
104 with benzene. These interferences may have various causes, and highlight the following:

105

106 For a substance to act as an interfering agent, it must have a retention time in the chromatographic
107 column within the interval for the identification of benzene, so that both species reach the detector
108 within this interval.

109

110 If the above is true, the interference causes an increase or decrease in the detector signal. When
111 the chromatograph has a PID, one of the following occurs:

112

113   1. If any organic compound other than benzene is ionised by the radiation of the detector
114   lamp, the electronic density, and consequently the electrical signal, increase, which leads to
115   an increase in the concentration of benzene. For this, the ionization potential of the
116   interferent must be lower than that associated with the radiation of the lamp.

117

118   2. When the interferer causes a decrease in the benzene signal, there can be several causes:

119

120   2.1. The radiation of the detector lamp is absorbed to a greater or lesser extent by the
121   interferer, and the remaining energy is insufficient to completely ionise the benzene. This
122   phenomenon is known as the "quenching effect" (Chou 1999).This has also been described
123   and evaluated in a previous article (Romero et al.2017).

124

125   2.2. The interferer absorbs (blocks) part of the formed ions that participate in the
126   quantification of benzene, leading to decrease in the detected concentration. This
127   mechanism is known as quenching effect via electron capture. As discussed below,
128   tetrachloromethane (TCM) acts in this way.

129

130 The 2005 version of part 3 of the standard EN 14662 included a list of paraffinic, cyclic and
131 halogenated organic compounds (trichlorethylene and TCM) that should be tested as possible
132 interferers. In the 2015 version, all hydrogenated compounds are maintained, isooctane (2,2,4-
133 trimethylpentane) and 1-butanol have been added and TCM has been removed. Table 2 shows all
134 the common and specific components of each version.

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136   Table 2. Organic compounds used to assess interference in the measurement of benzene in air, in
137   accordance with standards EN 14662-3 (2005 and 2015).

138

139   When we carried out the interference tests, part 3 of the standard (2005) was still current and the
140   Type Approval Test was carried out as indicated, where the established benzene concentrations
141   were close to 0.5 $\mu g/m^3$ and 40 $\mu g/m^3$. For these concentrations, benzene measurements were
142   compared in the absence and presence of the interfering agent (table 2). We observed that the
143   presence of the interfering agent did not affect the smaller benzene concentrations (approximately
144   0.5 $\mu g/m^3$) but the highest concentrations decreased significantly, up to a third of its value.

145

146   Locoge et al (2010) used the same chromatograph, obtaining the chromatograms as shown in figure
147   1, and observed the following:

148

149   1. Peak 2, which was within the interval that quantified benzene, also contained the following
150   compounds: cyclohexane, 2-methylhexane, 2,3-dimethyl pentane and TCM.
151   2. The first three cited interferers increased the concentration of benzene because their
152   respective ionisation potentials (between 9.88 and 10.08 eV) were lower than the potential
153   generated by the detector lamp (10.6 eV), and therefore the electric intensity in the
154   detector increased, leading to an increase in the apparent concentration of benzene.
155   3. TCM exhibited different behaviour as its ionisation potential (11.7 eV) was greater than
156   that emitted by the lamp; therefore it does not ionise or increase the intensity in the
157   detector. However, it is evident that it acts in an inverse manner, since it significantly
158   decreased the apparent benzene concentration.

159
160

161   Figure 1. Benzene chromatogram with the organic compounds described in the standard as
162   potential measurement interferers.

163

164   The aim of this article was to study the cited behaviour of TCM. First, the possible presence of this
165   compound in air that can lead to high deviations in benzene concentrations was studied. Second, a
166   mechanism was proposed to explain the aforementioned deviations.

167

168   The synthesis of TCM for direct use is prohibited by the Montreal Protocol because it is a substance
169   that destroys the ozone layer. However, its use as a raw material for the synthesis of other
170   substances such as hydrofluorocarbons (HFC), pyrenthroid pesticides or perchloroethylene is
171   allowed (Graziosi et al, 2016). Diffuse emissions may occur in its manufacture or during its use in
172   the aforementioned syntheses. In this sense, Penny et al (2010) estimated in 2007 emissions of,
173   approximately, 9500 MT of TCM in 192 countries. However, since the entry into force of the
174   Montreal Protocol, there has been a progressive decrease in the environmental presence of TCM,
175   with a decrease in the global average concentration of 10 to 15 pptv / decade (equivalent to 69 to
176   104 ng/Nm^3/decade). In 2005, Agency for Toxic Substances and Disease Registry (2005) determines
177   a global average concentration of 0.7 $\mu g/Nm^3$ with peaks in urban areas of 1.4 to 4.5 $\mu g/Nm^3$ and
178   Brosas (2008) detected 45 $\mu g/Nm^3$ in the vicinity of landfills. Most recent data provided by Blas et
179   al. (2016) in diverse cities of the world confirm average values of 0.61 $\mu g/Nm^3$ in Lukang (Taiwan),

180 $\underline{0.64\ \mu g/Nm^3}$ in Bristol (UK) and 1.10 µg/Nm³ in Bilbao (Spain). In this last city, maximum
181 concentrations of 9.94 µg/Nm³ have been measured. These values justify the concentrations that
182 have been used in the tests carried out in this work. It should also be noted that the TCM has a half-
183 life in the troposphere from 26 to 35 years (SPARC, 2013; Liang et.al, 2014), so its effects, such as
184 the one indicated here, will be manifested during the next two decades.

185
186
187 **EXPERIMENTAL**
188
189 **Test atmosphere:** A standard atmosphere system was used, which allowed "zero" air, and mixtures
190 of air with benzene and/or TCM with known concentrations, at a temperature of 20±2 ^{o}C, pressure
191 of 1013 hPa and 50% relative humidity.
192
193 The airflows containing the components of interest (benzene and TCM) were prepared as in the
194 installation shown in figure 2, which consisted of the following:
195
196 • **Initial air:** Ambient air was obtained from a compressor free of lubrication oil to avoid air
197 pollution with organic volatiles contained in the oil (the compression chamber was made of
198 polytetrafluoroethylene (Teflon®), which did not require lubricant oil). The compressor dried the air
199 to 5% relative humidity, providing an adjustable pressure controller at the outlet that was
200 maintained at 1.8 bars.
201
202 • **"Zero" air purification and humidification:** After leaving the compressor, the air passed through
203 several beds containing silica gel, active carbon and alumina that almost completely dried it and
204 eliminated possible traces of organic and other inorganic contaminants (mainly nitrogen dioxide
205 and other acidic gases). After purification, the concentration levels of the organic pollutants in
206 "zero" air were periodically checked by chromatographic analysis, ensuring they were below the
207 limits of chromatographic detection. The airflow, up to a maximum of 200 L/min at atmospheric
208 pressure, was regulated with a Bronkhorst HI-T mass controller (B HI-T), depending on the required
209 concentrations of the components for each test.
210
211 Figure 2. Diagram of the standard atmosphere installation used to obtain airflows with benzene
212 and/or TCM at known concentrations
213
214 After purification, the airflow was humidified to a relative humidity of 50±5%, which was constant
215 for all tests, given its effect on the results. To humidify the airflow, the air conduction behind the
216 compressor was bifurcated: one through which dry air circulated and another that was connected
217 to a humidifier, until reaching airflow saturation. The regulation of both flow rates (dry and wet)
218 was ensured using two B HI-T mass controllers. Both lines were rejoined to obtain the final required
219 moisture level, measured with a hygrometer. The flow rate of water vapour supplied to the air after
220 the humidifier was calculated.
221
222 • **Incorporation of pollutants into the "zero" air stream:** The pollutants (benzene and TCM) mixed
223 with nitrogen were stored in bottles at certified concentrations, which were connected to the

224   humidified "zero" air line. The concentrations of benzene in the two bottles were 335 µg/m^3 and
225   1054 µg/m^3. The concentrations of TCM in the two bottles were 17.6 µg/m^3 and 65.3 µg/m^3.
226
227   The final standard concentration of pollutant x (Cp$_x$, expressed in µg/m^3) after mixing the flows of
228   the bottle/s and the air was determined from the mass balance as:
229
230                            $Cp_x = Q_{bx} . Cpb_x/(Q_a + \Sigma Q_b)$ Eq. (1)
231
232   where Cpb$_x$ is the concentration of x in the bottle of origin, Qb$_x$ is the flow of the bottle containing
233   pollutant x, and Q$_a$ is the humidified "zero" air flow and ΣQ$_b$ is the sum of the flows, respectively.
234
235   The above concentrations and flow rates were under the reference conditions of temperature and
236   pressure, 293 K and 101.3 KPa, respectively. These conditions were maintained at the entrance of
237   each chromatograph for all tests. There was a barometer in the laboratory, and high sensitivity
238   manometers were connected to the input of each chromatograph to maintain the flow at the
239   reference pressure.
240
241   In order to maintain the air currents at the reference temperature (20±2 ^{o}C), the above-described
242   installation and the chromatographs were placed in respective chambers equipped with thermal
243   conditioning.
244
245   Two Syntech Spectras GC955 (Groningen, Netherlands) chromatographs were used. These are
246   widely used in European air pollution monitoring networks, and were identified as analysers I and
247   II.
248
249   The analytical process was semi-continuous. While the analyser was analysing a sample, a new one
250   was sampled and sent to the pre-concentration system.
251
252   The procedure is described in the following stages:
253
254   • The air sampling system comprised a 35 mL capacity piston pump, with 175 mL aspiration, and
255   the suction operation was repeated five times. The successive 35 mL samples of air moved to a pre-
256   concentrator (consisting of a column filled with Tenax), which retained the organic compounds and
257   released the excess air.
258
259   • Once the five suction cycles were completed, the contaminants retained in the pre-concentrator
260   underwent thermal desorption and were pulled with Nitrogen 5.0 (as a carrier gas) towards the
261   chromatographic column. The column was 15 m in length and 0.32 mm in diameter, and was
262   formed of silica with a film of adsorbent polymer (1 µm heliflex coating) for substances with boiling
263   points between 40 and 250 ^{o}C. The initial oven temperature was set at 50 ^{o}C and maintained for 3
264   min, then increased to 70 ^{o}C at 10 ^{o}C/min. This temperature was maintained for 7 min before being
265   reduced to 50 ^{o}C with a cooling rate of 10 ^{o}C/min.
266
267   • To explain the behaviour of benzene in the PID, we proposed the model shown in figure 3, which
268   also served as a basis to determine what happens in the presence of TCM (figure 5). When the

269 gasified benzene (n, in molar units) leaves the column, pulled by the carrier gas, it accesses the PID
270 where a fraction, F (≤1), is ionised by the radiation of the lamp, forming nF ionic couples (electrons
271 and benzyl cations). This forms a magma that produces an electrical intensity when passing through
272 the electrodes of the detector, whose area is proportional to the concentration of benzene in the
273 sample, given that F is practically constant within the range of concentrations tested, as
274 demonstrated by the experimental results. The benzyl ions recover the electrons in the cathode
275 and benzene is reformed, hence the non-destructive nature of the detector.

277 • The "windows" used to quantify the benzene in chromatographs I and II used, were 176–212 s
278 and 148–182 s, respectively.

280 Figure 3. Model of the behaviour of benzene in the PID of the chromatograph in the absence of
281 TCM.

283 Each analytical determination (from the first aspiration of air to the final result of the detected
284 concentration) occurred in 15 min.

286 The measurements were obtained using the following sequence:

288 • A continuous flow of "zero air" was prepared with the relative humidity, temperature and
289 standard pressure mentioned above. The chromatographic analysis of at least three samples of air
290 was performed until free of organic components.

292 • Once the absence of contaminants was verified, the flow of benzene was added to the "zero" air
293 from their respective bottles and, where appropriate, the TCM. Flows were previously calculated to
294 obtain the final concentrations required in the tests. In each experiment, at least six samples were
295 taken after measuring the stabilities of the concentration levels, and the average was determined.

298 **RESULTS AND DISCUSSION**

300 According to the standard EN 14662, the parameters used to evaluate the deviations caused by the
301 interferers were:

303 • Effect of organic compounds, b_{Corg}:

305 $$b_{Corg} = \left| C_{aCorg} - C_a \right| / C_a \quad \text{Eq. (2)}$$

307 where C_{aCorg} is the average concentration of benzene chromatographic measurements in the
308 presence of organic compounds ($\mu g/m^3$) and C_a is the average concentration of individual benzene
309 measurements in the absence of organic compounds ($\mu g/m^3$).

313 • The typical uncertainty, U_{Corg}:

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315 $$U_{Corg} = \mid C_{aCorg} - C_a \mid / \sqrt{3} \quad \text{Eq. (3)}$$

316

317 • The test value, V_{test}:

318 $$V_{test.} = (U_{Corg} / C_a) \cdot 100 \quad \text{Eq. (4)}$$

319

320

321 We have included the relative error (RE):

322

323 $$RE = b_{Corg} \cdot 100 \quad \text{Eq. (5)}$$

324

325 **Previous experiments**

326

327 First, the organic interference tests were carried out. These tests have been established in the
328 earlier version of part 3 of the standard EN 14662, and involve comparing the responses of the
329 chromatographs when analysing standards (C_p) containing benzene at two concentrations (one-
330 tenth of the limit value established in the European legislation, Directive 2000/69/CE, and close to
331 70–90% of the maximum certification range) and mixtures of benzene and the organic compounds
332 indicated in table 3, each with concentrations close to 10 $\mu g/m^3$. The results are shown in table 3
333 using the previously defined parameters.

334

335 In each test, six individual measurements were made to obtain statistically significant data, using
336 the arithmetic mean as a representative value (C_b).

337

338 Table 3. Results obtained in the tests for the interference of organic compounds in benzene for
339 analysers I and II, with respect to those established in part 3 of the standard EN 14662.

340

341 As shown in table 3, the mixture of organic compounds interfered significantly, causing errors close
342 to 60% for the highest concentrations of benzene in the two chromatographs tested.

343

344 Based on the results, an analogous test was performed for concentrations of benzene close to the
345 limit value established in the Community Legislation (5 $\mu g/m^3$). The results are shown in table 4.

346

347 Table 4. Results for the test of the interference of organic compounds in benzene for analysers I
348 and II, for benzene concentrations close to the limit value in Europe.

349

350 The results also showed the interference of the mixture of organic compounds on the readings of
351 benzene concentration, though in this case the deviations were different for each chromatograph.

352

353 Due to the different behaviours of organic compounds that reach the PID in the benzene "window"
354 (see Background and Objectives), separate studies should be carried out for those that positively
355 (increasing) and negatively (decreasing) affect the concentration of benzene. TCM caused the
356 concentration of benzene to decrease, and was interferer studied in this article.

357

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359 **Effect of TCM on benzene measurement**

360

361 To study the effect of TCM on the chromatographic measurements of benzene, the analyzer was
362 first calibrated (C_a versus C_p) to standard concentrations (C_p) of the pollutant, approximately 0, 2.5,
363 5, 10, 20 and 40 $\mu g/m^3$.

364

365 Next, air flows containing benzene were prepared at the same concentrations but with the addition
366 of TCM flows diluted with nitrogen, such that the final concentrations of TCM (C_{TCM}) were 0.5, 1.0,
367 2.0 and 5.0 $\mu g/m^3$, leading to the chromatographic reading (C_{aTCM}). The TCM concentrations were
368 selected due to the presence in urban areas at these levels (section 2), allowing estimations of the
369 possible deviations in expected benzene measurements. To establish the concentrations of the
370 benzene and TCM standards in the test chamber shown in table 5, the proportions of the different
371 streams (zero air, and the benzene and TCM bottles diluted with nitrogen) have been taken into
372 account, and in this case, equation 1 was applied. In all cases, each measurement was repeated six
373 times and the standard deviations of each measurement are indicated in parentheses.

374

375 Table 5. Concentrations of benzene without TCM (C_a) and with TCM (C_{aTCM}), measured by analyzer I
376 for different concentrations of TCM

377

378 From the results in table 5, the presence of TCM significantly decreased the benzene concentration
379 readings with respect to the standards, and the deviations increased with TCM concentration.
380 Likewise, for the same TCM concentration, the relative errors of the readings at different standard
381 benzene concentrations remained practically constant.

382

383 The experimental values of C_a and C_{aTCM} versus C_p of table 5 are shown in figure 4, and the following
384 was observed:

385

386 1. The relationship between C_a or C_{aTCM} and C_p for each series was linear (p<0.001) and passed
387 through the origin of the coordinates, leading to the following general equations:

388

389 $$C_a = K^* \, C_p \text{ (without TCM) Eq. (6)}$$
390 $$C_{aTCM} = K \, C_p \text{ (with TCM) Eq. (7)}$$

391

392 where K^* and K are the slopes of the respective straight lines.

393

394 2. The slopes of the straight lines decreased with increasing TCM concentration.

395

396 Figure 4. Representation of benzene concentrations, C_a and C_{aTCM}, read by analyser I, compared
397 with the introduced patterns, C_p, at different TCM concentrations.

398

399 Table 6 shows the adjusted equations of the experimental values in table 5. A decrease in K was
400 observed as the concentration of the interferent increased.

401

402 Table 6. Adjusted equations for the obtained experimental values.

403

404   To attempt to explain what occurs in the PID, and find the best relationship in terms of K for TCM
405   concentrations, we proposed the model in figure 5. The sequence and behaviour of the two
406   analysed species are depicted as they pass through the detector. The basic concepts of the model
407   are as follows:

408

409   1. The air sample, containing benzene (n moles) and TCM (m moles), accesses the PID. The lamp
410   ionises a fraction F of benzene but does not act on the TCM, since its ionisation potential is greater
411   than that provided by the lamp.

412

413   2. When the magma is formed, the mechanisms that take place are complex, given that the
414   electrons formed by benzene ionisation (nF) are distributed between two competing paths. One
415   part (pF) is directed towards the anode of the detector, and the other (qF) is retained by the strong
416   electronegativity of TCM. Thus, the measurement by the detector (pF) depends on the electric
417   fields configured by both systems and the quantities of benzene (n) and TCM (m). This may cause
418   one of the species to be limiting, this is that one of them is in default with respect to the other,
419   which also affects the distribution.

420

421   3. Finally, the system changes as shown in figure 5. The electric circuit closes and the initial species
422   is regenerated, showing that the PID is non-destructive in nature.

423

424   Figure 5. Simplified model of the behaviour of benzene and TCM when interacting simultaneously
425   in the PID detector

426

427   From a quantitative point of view, the proposed model and experimental data and establish the
428   following:

429

430   • According to figure 3, the concentration of benzene read by the chromatograph in the absence of
431   TCM (C_a) is expressed by:

432

433 $$C_a = C_p = n.F.M_b /V_T = n.F.\alpha_b \qquad \text{Eq. (8)}$$

434

435   where M_b is the molecular mass of benzene, V_T is the volume of the air sample and $\alpha_b = M_b/V_T$.

436

437   • As explained previously, when benzene and TCM simultaneously coexist, the benzene
438   concentrations read by the chromatograph (C_{aTCM}) for a given concentration of TCM, followed the
439   generic representation in figure 6, the following equation was confirmed:

440

441 $$C_{aTCM} = K.C_p = C_p - \Delta \qquad \text{Eq. (9)}$$

442

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

444

445   Figure 6. Generic representations of benzene concentrations (C_a and C_{aTCM}) read by the
446   chromatograph with respect to the standard concentrations (C_p)

447

448 As can be deduced from figures 4 and 6, Δ was proportional to C_p for each C_{TCM}, and was also
449 dependent on C_{TCM}, which was determined experimentally. Based on the above, the following
450 function was proposed:

451 $$\Delta = C_p . \varphi(C_{TCM}) \qquad \text{Eq. (10)}$$

452

453 • Based on figures 5 and 6 and equations 9 and 10:

454

455 $$C_{aTCM} = p.F.\alpha_b = (n - q).F.\alpha_b = C_p - q.F.\alpha_b = C_p - \Delta = C_p - C_p.\varphi(C_{TCM}) = [1 - \varphi(C_{TCM})].C_p \quad \text{Eq. (11)}$$

456

457 From equations 9 and 11:

458 $$1 - K = \varphi(C_{CTM}) \qquad \text{Eq. (12)}$$

459

460 Table 6 shows the values of $1 - K$, which correlated with the respective TCM concentrations. The
461 best fit is represented by the following equation:

462

463 $$1 - K = 0.389.C_{TCM}^{0.388} \quad (r^2 = 0.988) \quad \text{Eq. (13)}$$

464

465 From equations 9, 11 and 13:

466 $$C_{aTCM} = (1 - 0.389.C_{TCM}^{0.388}) \, C_p \quad \text{Eq. (14)}$$

467 From equation 14, the relative error of the benzene chromatographic measurements in the
468 presence of TCM (RE) can be estimated:

469

470 $$RE = [(C_{aTCM} - C_p)/C_p].100 = (0.389.C_{TCM}^{0.388}).100 \qquad \text{Eq. (15)}$$

471

472 Thus, for TCM concentrations of 0.7, 1.4 and 4.5 µg /m^3 (levels that are currently found in urban
473 areas), errors may occur in benzene readings close to 34, 44 and 70%, respectively. These
474 deviations are high and not acceptable.

475 As indicated in the standard EN 14662:2005, TCM was included as a possible interfering
476 contaminant to be evaluated, but was not included in the new version. However, section 8 of the
477 current standard establishes that *"some compounds, including carbon tetrachloride or butanol, may
478 be present under site-specific conditions. In such cases, the responsibility for the proper
479 determination of benzene falls on the network that operates the analyzer by the appropriate choice
480 of separation conditions (analytical column, temperature program of the column)"*. This approach
481 seems difficult for network managers to implement, and we feel that the manufacturers of the
482 equipment should be responsible for solving this problem since they have the required technology
483 and equipment.

484 Therefore, a forum should be opened to discuss this problem, given that the GC-PID equipment is
485 the most widely used in the EU for the measurement of benzene in air and it would be advisable to
486 determine the best way to resolve this issue.

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CONCLUSIONS

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488 1. Given the toxic characteristics of benzene, the EU has established that its determination in
489 ambient air is mandatory, particularly in urban areas. Benzene forms part of automotive fuels and is
490 also present during the combustion of these fuels, leading to the establishment of an annual
491 average limit value of 5 µg/m^3. GC-PID has also been confirmed as the reference technique for the
492 detection of benzene, as described in the standard EN 14662:2005. This standard comprises three
493 parts. Part 3 was modified in 2015, and describes the tests (so-called Type Approval Tests) that
494 must be conducted and passed by the automatic measurement equipment before being marketed
495 in EU countries. One such test verifies whether organic compounds that are common in ambient air
496 interfere with the measurement of benzene, including TCM. This compound was considered in the
497 earlier 2005 version of the standard but was excluded from the new 2015 version.

498 2. The research described in this article determined that the measurement of benzene by GC-PID in
499 the presence of TCM caused a significant decrease in the concentration of benzene. The relative
500 error (RE) of the concentration of benzene measured as a function of the concentration of TCM
501 (C_{TCM}) can be calculated from the following expression:

502 $$RE = (0.389 \cdot C_{TCM}^{0.388}) \cdot 100$$

503 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),
504 the REs in benzene concentration would be 34 and 70%, respectively, which are independent of the
505 concentration of benzene.

506 3. Given the importance of this behaviour, a possible mechanism was proposed to explain the
507 phenomenon when benzene is measured in the presence and absence of the interferent.

508 4. Of note, it is established in part 3 of the standard EN 14662:2015 that the managers of the air
509 pollution monitoring network are responsible for determining the presence of TCM in the area
510 where the atmospheric pollutants are measured. If detected, they must act to eliminate the effect
511 of the interferent. We believe that the manufacturers of the chromatographs have greater
512 technical and scientific capacity to solve this issue than the network managers.
513
514 This study highlights the uncertainty of measuring benzene using a GC-PID, and it is important to
515 open a forum for discussion of this issue.
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607   Table 1. Contribution of the main anthropogenic sources of benzene in Europe.

Source	Percentage (%)
Vehicles	80-85
Oil refineries	0.3-1.5
Fuel distribution	2.6-6
Chemical industry	1.3-13
Domestic heating	3-7
Use of solvents	1-4

608

609   Table 2. Mixture of organic compounds to assess interferences in the measurement of benzene in
610   air, in accordance with standards EN 14662-3 (2005 and 2015).

EN 14662-3:2005	EN 14662-3:2015
Methylcyclopentane	
2,2,3- Trimethylbutane	
2,4-Dimethylpentane	
Cyclohexane	
2,3-Dimethylpentane	
2-Methylhexane	
3-Ethylpentane	
Trichlorethylene	
n-Heptane	
Tetrachloromethane	1-Butanol
	2,2,4-Trimethylpentane

611

612   Table 3. Results obtained in the test of the interference of the organic compounds in the benzene
613   readings for the analyzers I and II, according to what is established in part 3 of the standard EN
614   14662.

ANALYZER I					
Standard concentrations introduced		C_b ($\mu g/m^3$)[1]	RE (%)	U_{Corg} ($\mu g/m^3$)	V_{test} (%)
C_p C_6H_6 ($\mu g/m^3$)	C_p organic compounds ($\mu g/m^3$)				
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)	60.71	11.59	35.05
32.55	10.00	C_{aCorg}: 13.00 (1.05)			
ANALYZER II					
Standard concentrations introduced		C_b ($\mu g/m^3$)[1]	RE (%)	U_{Corg} ($\mu g/m^3$)	V_{test} (%)
C_p C_6H_6 ($\mu g/m^3$)	C_p organic compounds ($\mu g/m^3$)				
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)	60.56	13.84	34.97
39.50	10.00	C_{aCorg}: 15.61 (0.36)			

615   [1]The parenthesis shows the standard deviation of the 6 measurements.

616

617

618 Table 4. Results obtained in the test of the interference of organic compounds in the benzene
619 readings of analyzers I and II for benzene concentrations close to the limit value in Europe.

620

ANALYZER I			
Standard concentrations introduced		C_b $(\mu g/m^3)^1$	RE (%)
C_p C_6H_6 $(\mu g/m^3)$	C_p organic compounds $(\mu g/m^3)$		
4.68	0.00	C_a: 4.64 (0.02)	
0.00	10.00	0.05 (0.00)	69.2
4.68	10.00	C_{aCorg}:1.43 (0.08)	
ANALYZER II			
Standard concentrations introduced		C_b $(\mu g/m^3)^1$	RE (%)
C_p C_6H_6 $(\mu g/m^3)$	C_p organic compounds $(\mu g/m^3)$		
5.06	0.00	C_a: 5.03 (0.17)	
0.00	10.00	0.05 (0.00)	40.4
5.06	10.00	C_{aCorg}:3.00 (0.01)	

621 [1]The parenthesis shows the standard deviation of the measurements.

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649   Table 5. Concentrations of benzene without TCM (C_a) and with TCM (C_{aTCM}), read by Analyzer I for
650   different concentrations of TCM.
651

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
42.60	42.57 (0.28)	31.32 (0.16)	26.42
Series II: C_{TCM} = 1.0 μg/m^3			
C_p C_6H_6 (μg/m^3)	C_a (without TCM) (μg/m^3)	C_{aTCM} (with 1 μg/m^3 de TCM) (μg/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 μg/m^3			
C_p C_6H_6 (μg/m^3)	C_a (without TCM) (μg/m^3)	C_{aTCM} (with 2 μg/m^3 de TCM) (μg/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 μg/m^3			
C_p C_6H_6 (μg/m^3)	C_a (without TCM) (μg/m^3)	C_{aTCM} (with 5 μg/m^3 de TCM) (μg/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

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658   Table 6. Adjusted equations of the experimental values obtained.

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
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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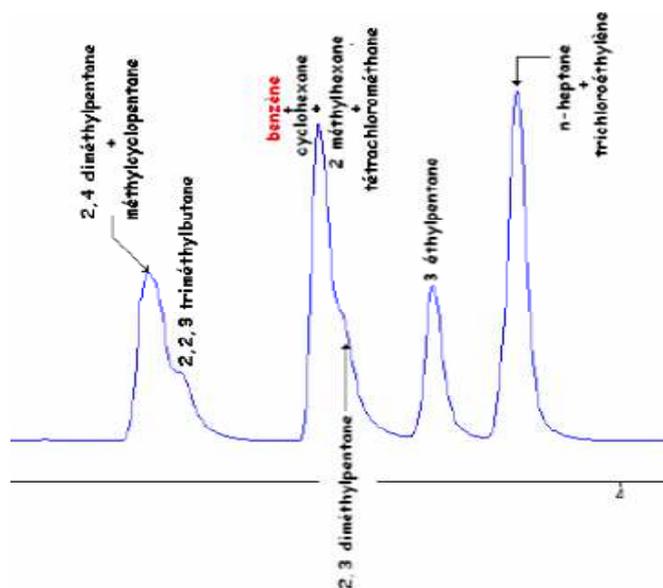
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677   Figure 1. Benzene chromatogram with the organic compounds considered in the standard as
678   possible interferences in the measurement. (Locoge et al.,2010)
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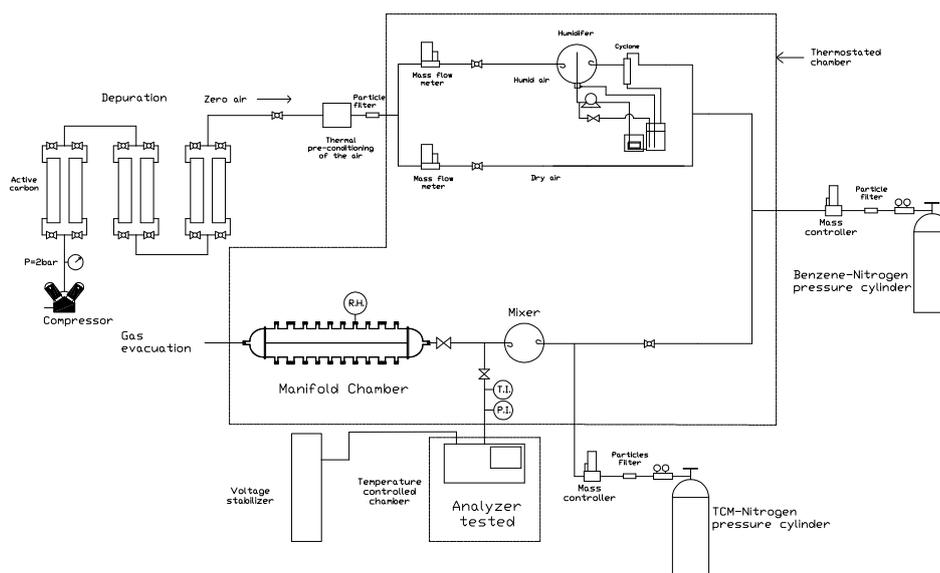
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684   Figure 2. Diagram of the components of the standard atmosphere installation used to obtain air
685   flows with benzene and/or TCM at known concentrations.
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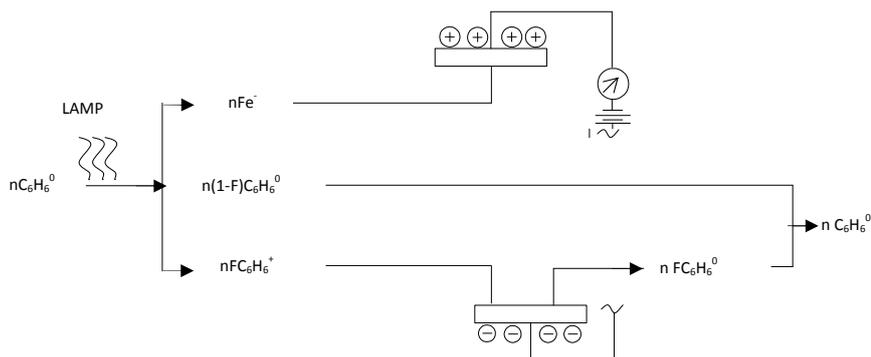
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689   Figure 3. Behaviour model of benzene in the PID of the chromatograph in absence of TCM.
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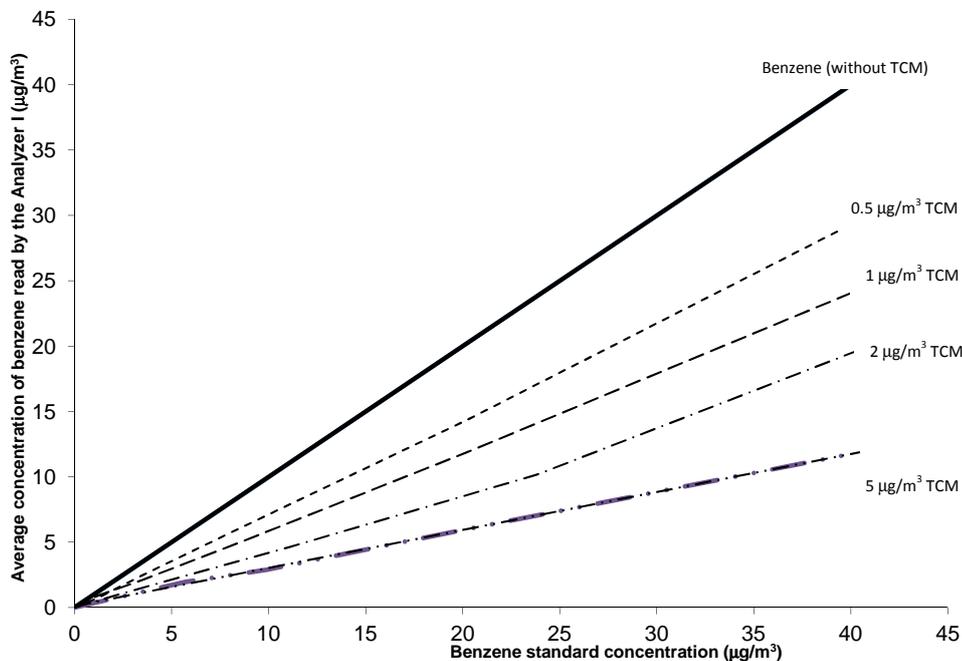
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693   Figure 4. Analyzer calibration lines for benzene without and with various concentrations of TCM.
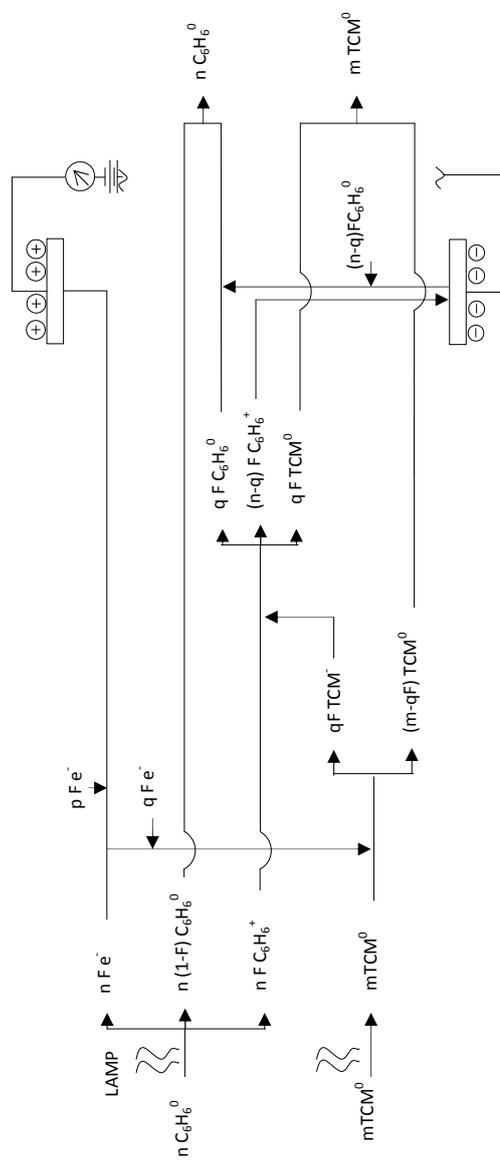
Figure 5. Simplified model of the behavior of benzene and TCM when they interact simultaneously in the PID detector.

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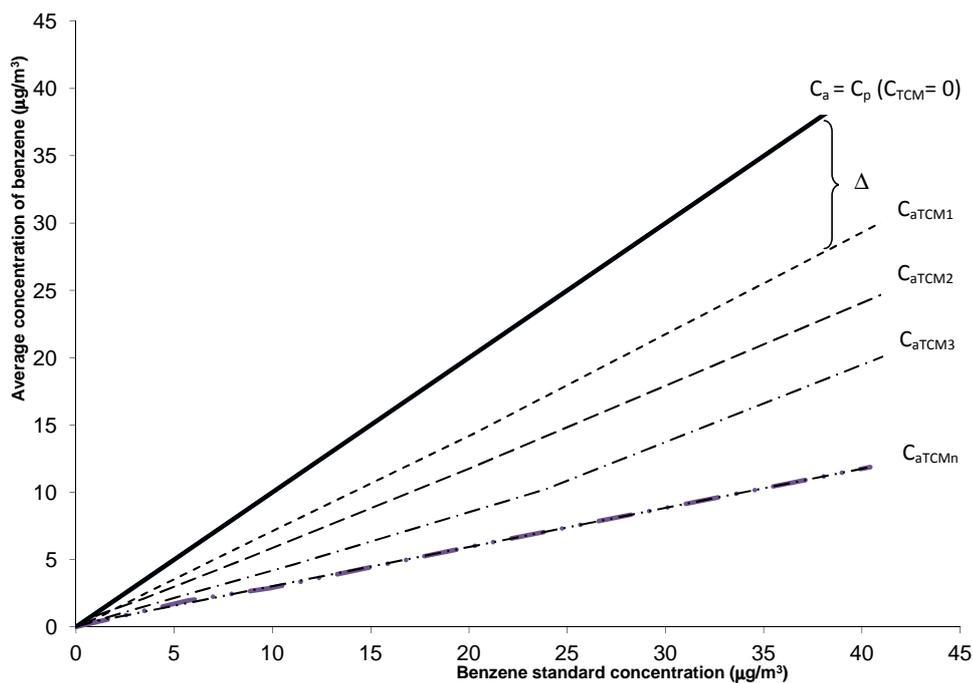
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2   Figure 6. Generic representations of benzene concentrations read by chromatograph (C_a and
3   C_{aTCM}) with respect to the standard concentrations introduced (C_p).
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