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A New Perspective on Hydrogen Chloride Scavenging at High Temperatures for Reducing the Smoke Acidity of PVC in Fires. III: EN 60754-2 and the species in solution affecting pH and Conductivity

Iacopo Bassi, Claudia Bandinelli, Francesca Delchiaro and Gianluca Sarti *

Reagens S.p.A., Via Codronchi, 4, 40016 San Giorgio di Piano, Italy; iacopo.bassi@reagens-group.com (I.B.); claudia.bandinelli@reagens-group.com (C.B.); francesca.delchiaro@reagens-group.com (F.D.)
* Correspondence: gianluca.sarti@reagens-group.com

Abstract: The combustion of PVC cables in fires results in the release of hydrogen chloride gas. In the European Union, Regulation (EU) No 305/2011, in force since 2017, requires the classification of cables permanently installed in buildings for reaction to fire, smoke, flaming droplets, and acidity. The additional classification for acidity is evaluated through EN 60754-2, involving pH and conductivity measurements. This study focuses on the essential research and development of low-smoke acidity PVC compounds for cables, mainly aiming to meet the stringent additional classifications for acidity, a1 or a2, which cannot be achieved with traditional PVC cables. Understanding the chemistry of thermal decomposition and combustion, especially in the presence of hydrogen chloride scavengers, is crucial for meeting the best acidity classification. The article reviews the current tube furnace tests used in the European Union for cable halogen and acidity assessments. It discusses the limitations of the existing method (EN 60754-2) and highlights the potential of emerging tests such as IEC EN 60754-3, which employs ion chromatography for improved sensitivity and specificity. In the experimental part of the article, various standard and low-smoke acidity cable compounds are tested using tube furnace experiments with different heating regimes. The concentrations of cations and anions in solution are measured through ion chromatography and inductively coupled plasma–optical emission spectrometry. This detailed analysis aims to identify the species influencing pH and conductivity, which is crucial for designing effective acid scavengers that do not impact conductivity. The conclusive results emphasize that HCl from PVC thermal decomposition is the primary driver of pH and conductivity, and the contribution from the decomposition of additives and byproducts from combustion is found to be negligible in most of the tested PVC compounds for cables. The findings underscore the importance of understanding the thermal decomposition of PVC compounds to design acid scavengers capable of trapping hydrogen chloride without adversely impacting conductivity.

Keywords: acid scavengers; PVC; cables; smoke acidity; hydrogen chloride; EN 60754-1; EN 60754-2; EN 60754-3; ion chromatography; PVC cables

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1. Introduction

1.1. Main Acidity Tests for Cables in the European Union (EU) and the Application Field

In the EU, several tests are used for assessing the corrosivity and acidity of fumes released from cables in case of fire. Tables 1 and 2 show the main ones and their current status.

Table 1. Standards used for detecting halogen and acidity/corrosivity of the smokes in the EU, their status, the product standard impacted by them, their current status, and test apparatus.

EU Standard	Use	Product Standard	Current Status	Test Apparatus
EN 60754-1:2014 +A1:2020 [1]	Assessment of halogens[1]	EN 50525-1:2011/A1:2022 Annex B [8], EN 50620 [9], EN 50618 [10]	Active	Furnace tube, titration
EN 60754-2:2014 +A1:2020 [2]	Assessment of halogens[1]	EN 50525-1:2011/A1:2022 Annex B, EN 50620, EN 50618	Active	Furnace tube, pH, conductivity
EN 60754-2:2014 +A1:2020	Additional classification for acidity	EN 50575:2014+A1:2016 [11]	Active	Furnace tube, pH, conductivity
EN IEC 60754-3:2019 [3]	Additional classification for acidity	EN 50575:2014+A1:2016	Under evaluation	Furnace tube, Ion Chromatography
EN 50267-2-1 [4]	Assessment of halogens[1]	EN 50525-1:2011 [12] Annex B	Withdrawn in 2022[1]	Furnace tube, titration
EN 50267-2-2 [5]	Assessment of halogens[1]	EN 50525-1:2011 Annex B	Withdrawn in 2022[1]	Furnace tube, pH, conductivity
IEC 60684-2 [6]	Assessment of halogens[1]	EN 50525-1:2011/A1:2022 Annex B	Active	F^- Selective Electrode
EN 50267-2-3 [7]	Additional classification for acidity before 2014	EN 50575:2014	Withdrawn in 2022[1]	Furnace tube, pH, conductivity

[1] EN 50267-2-1 and EN 50267-2-2 were referenced in EN 50525-1:2011, annex B. However, they were withdrawn in 2022. In the integration of EN 50525-1:2011, EN 50525-1:2011/A1:2022, EN 60754-1, and EN 60754-2 are mentioned instead.

Table 2. Some standards used for detecting halogen and acidity/corrosivity of the smoke in the EU: active versions and link with IEC standards.

IEC standard	EN standard	Amendments	Amendments
IEC 60754-1:2011	EN 60754-1:2014	EN 60754-1+A1:2019	EN 60754-1+A1:2020
IEC 60754-2:2011	EN 60754-2:2014	EN 60754-2+A1:2019	EN 60754-2+A1:2020
IEC 60754-3:2011	EN IEC 60754-3:2019		

Some of the standards mentioned in Table 2 are required by Regulation (EU) n. 305/2011 (Construction Product Regulation, or CPR) [13] for assessing the additional classification for acidity. EN 60754-2 is the standard required by EN 13501-6 [14] and EN 50575 to assess the additional classification for acidity requested in cables permanently installed in buildings, according to CPR. It is carried out in a furnace tube in isothermal conditions, where a test specimen of 1 mg is burnt for 30 minutes. The smoke is collected in some bubblers containing double-deionized water (DDW), and its pH and conductivity are measured. Three acidity classes can be determined depending on pH and conductivity, as indicated in Table 3.

Table 3. Additional classification for acidity. Requirements indicated in EN 13501-6. pH and Conductivity must be measured through EN 60754-2. .

Additional classification for acidity	pH	Conductivity [mS/mm]
a_1	> 4.3	< 2.5
a_2	> 4.3	< 10
a_3	≤ 4.3	≥ 10

Other standards in Table 2 function as tools for evaluating halogens, as outlined in Annex B of EN 50525-1. This European Standard establishes the general requirements for energy cables with rated voltages up to and including 450/750 V (U0/U) for power installations, domestic applications, and industrial appliances. Halogen-free materials must comply with the criteria in Annex B as a prerequisite for their use in specific product standards. That includes entries within the EN 50525 series for low-voltage electric cables and standards like EN 50620 for charging cables for electric vehicles and EN 50618 for electric cables in photovoltaic systems.

1.2. Main Acidity Tests for Cables in the EU

EN 50267-2-1, as his sibling EN 60754-1, aims to determine the amount of halogen acid gas released during the combustion of compounds for cables, excluding hydrofluoric acid. They are carried out using a tube furnace with a heating regime of 40 +/-5 min to 800°C and a further 20 +/-1 min at 800 +/- 10°C. They measure halogen acid content expressed in mg/g dissolved in bubbling devices containing 0.1 M solution of NaOH. The determination of halogen gas content is based on Volhard's method for detecting chlorine and bromine in aqueous solutions. An aliquot of 200 mL of the solution of the bubblers is collected in a flask with an excess of $AgNO_3$. The following reaction 1 takes place:

$$Ag+ (aq) + Cl– (aq) \rightarrow AgCl(s) \quad (1)$$

The excess of Ag+ is back-titrated with sodium, potassium, or ammonium thiocyanate in the presence of Fe^{3+}, according to reaction 2:

$$Ag+ (aq) + SCN– (aq) \rightarrow AgSCN(s) \quad (2)$$

The endpoint becomes evident when the dark-red complex of Fe(III) is formed (reaction 3).

$$Fe^{3+} (aq) + SCN– (aq) \rightarrow [FeSCN]^{2+} (aq) \quad (3)$$

Because the analytic method of EN 60754-1 is based on a titration of ions in solutions, which identifies the end point visually and involves many manual procedures, it does not have enough accuracy and precision for analytes at low concentrations, and it cannot be used when the halogen concentration is less than 5 mg/g. Furthermore, Volhard's method works for chlorine and bromine, but it is unsuitable for detecting fluorine because AgF is water soluble.

EN 50267-2-2, EN 50267-2-3, and EN 60754-2 intend to determine the acidity and corrosivity of effluents in case of combustion. They are carried out in a tube furnace in isothermal conditions at temperatures between 935 °C and 965 °C, where a test specimen of 1.000 +/- 1 g is burnt for 30 minutes. The smoke is collected in some bubblers containing DDW, and its pH and conductivity are measured. These standards lack specificity and cannot detect what species affect pH and conductivity, which can ingenerate some paradoxes highlighted in section 1.2.

IEC EN 60754-3 is performed as EN 60754-2 (same test apparatus, thermal profile, test time, and trapping solutions containing DDW) to detect halogen amounts from combustion. The solution of the bubblers is analyzed through an ion chromatography system (IC), performed according to ISO 10304-1, [15] to detect specifically fluorine, bromine, iodine and chlorine. The standard is suitable for detecting the concentration of halogens not exceeding 10 mg/g, with a limit of quantification (LOQ) < 0.1 % for each. The advantage of this standard is its remarkable sensitivity and specificity, combined with the low manual handling of the samples, which positively affects the repeatability of the measurements and the simultaneous detection of all halides in a single measure. This standard would resolve all problems in EN 60754-1, LOQ, accuracy, precision, specificity, and the number of manual procedures necessary to conduct the analysis, impacting time and repeatability. It also has the specificity EN 60754-2 does not have, identifying the actual species affecting pH and conductivity.

That is why IEC EN 60754-3 received some interest in standardization bodies as the best candidate for substituting EN 60754-2 in CPR and probably all the standards in Annex B of EN 50525-1.

1.3. pH and Conductivity Measures and Their Incongruences

If the solution's pH is directly linked to the acidity or basicity of the dissolved substances, the conductivity is only related to the concentration of electrolytes in there. Therefore, the conductivity increases only as the electrolytes in solution, basic, acidic, and neutral, rise in concentration, while pH decreases simply if the species are acidic and increases if basic. PVC compounds release hydrogen chloride (HCl) during combustion. HCl reaches bubbling devices, reducing pH and increasing the conductivity as its concentration rises. Theoretically, even neutral byproducts of the PVC compound combustion, like $MgCl_2$ and $ZnCl_2$, if they do not hydrolyze before, can evaporate at the test temperature of the standard. If so, they cannot affect pH but can impact the conductivity. Therefore, in a PVC compound, pH and conductivity can be affected by several reactions and if their byproducts can reach the bubblers. However, the PVC thermal decomposition through zip-elimination is crucial, bringing a massive quantity of HCl to the solutions. In other polymers, different things happen, depending on the nature of the polymer and its additives. For example, thermoplastic polyurethanes (TPU) are not inherently flame retarded as PVC, and they need flame retardants to improve fire performance to meet the requirements of specific standards in terms of reaction to fire. Melamine used in some intumescent systems as a component of flame retardant decomposes, emitting ammonia, which evolves during the combustion.

Ammonia affects pH but simultaneously increases the conductivity of the solutions in which fumes are dissolved. Contrary to PVC compound, in some flame retarded TPU, pH and conductivity increase simultaneously as the concentration of intumescent flame-retardant increases. The paradox in CPR is that some halogen-free compounds could bring basic solutions, but having a conductivity of more than 10 µS/mm, they would be in the worst "acidity" class, a_3. Sometimes, these paradoxes have been resolved in other standards with special derogation decided in the technical committees and the specific working groups. For example, halogen-free TPUs not capable of reaching a conductivity of lower than 10 µS/mm would be non-halogen-free compounds, according to Annex B of EN 50525-1. That is why in EN 50620, which regulates charging cables for electric vehicles and where mainly flame retarded TPU compounds are utilized in jackets, the limits of conductivity were increased from 10 µS/mm to 40 µS/mm to pass the assessment. In this case, the standard itself has been sized on the best technical achievement of the compound as the best compromise between fire performances, pH, and conductivity.

All these considerations highlight how knowing the species in the solutions of bubblers capable of affecting pH and conductivity is crucial for designing the proper compound composition.

1.4. Thermal Decomposition and Combustion of PVC Compounds

PVC compounds have a complicated pattern of thermal decomposition depending on the specific additives used to characterize them. For instance, a PVC compound for cables utilized for producing CPR cable can contain suspension PVC K70, a general purpose plasticizer (GPP) like DINP, a 70°C thermal stabilizer, filler like calcium carbonate, flame retardants such as antimony trioxide (ATO) and zinc borate, and flame retardant fillers like magnesium hydroxide (MDH) or aluminum trihydroxide (ATH). Ref. 16 describes in detail the thermal decomposition and combustion of such PVC compounds. Summarizing, two main stages are found. The first stage starts around 220 °C and ends at 350 °C. Here, HCl is released following the zip elimination of HCl, and polyene sequences are formed. They can arrange intramolecularly yielding benzene or intermolecularly bringing the matrix's crosslink. [17-21] In this stage, besides benzene, water from ATH, MDH, CO_2 from the reaction of $CaCO_3$ with HCl, and plasticizers are released in the gas phase. All HCl is released in the first stage. The second stage starts over 450 °C, where the crosslinked matrix releases moieties (mainly aliphatic hydrocarbons) and yields a black charred mass in the condensed phase. If the pattern of the thermal decomposition and combustion depends on the specific ingredients in the cable PVC compound, HCl will always be released between 220°C and 350°C.

Therefore, a good HCl scavenger must be efficient in the first stage to minimize the release of HCl in the gas phase from the PVC compound. However, also the "stability" of the reaction products coming from the acid scavenger must be high, avoiding decompositions or evaporation capable of affecting the pH and conductivity of the solutions in the bubblers according to EN 60754-2. Specifically, the reaction products must be stable up to 965 °C, i.e., the maximum temperature of that standard, and the species capable of affecting pH and conductivity should be carefully evaluated.

1.5. Scope of the article

The research on low smoke acidity PVC compounds for cable is inserted in the regulatory framework described in the following article [22].

According to CPR, exploring the concentrations of anions and cations in solution is crucial in researching and developing novel acid scavengers at high temperatures capable of capturing HCl evolving during the combustion of PVC compounds to meet the best additional classifications for acidity. The dosage of anions and cations allows us to verify all possible contributions to pH and conductivities from the PVC compounds' ingredients for cables. Some can evaporate, and others can decompose, releasing gasses affecting pH and conductivities.

In the paper, despite IEC EN 60754-3 and ISO 10304-1 stating that the standard should be used only at low-level halogen concentration, below 0.5 %, we verified that IC can be quickly and precisely used in PVC compounds also to detect halogens at higher concentrations than 0.5 % and even to dose other ions, potentially affecting pH and conductivity as halogens do. Therefore, specific methods based on tube furnace test apparatus, internal methods 4 and 5, were developed, described, and applied in the paper. The methods use the heating regime of EN 60754-2 and EN 60754-1, measure pH and the conductivity, and through IC and inductively coupled plasma–optical emission spectrometry (ICP-OES), detect anions and cations affecting the conductivity.

Furthermore, the article proposes a method to understand if the scavenging acts in the condensed phase without the contribution of substances evaporating in the gas phase and conveyed in the bubblers. From pH and conductivity measurements, there is the opportunity to understand whether the mechanism is in the condensed phase or if gas-phase reactions are activated, resulting in deviations from the Debye-Hückel-Onsager (DHO) equation for HCl solutions. The model is described in detail in Annex B.

2. Materials and Methods

2.1. Materials

Table 4 shows the first set of formulations. F50.0 represents the typical formulation for the PVC jacket compound used in low-voltage cables. All the other formulations in Table 4 are derived from F50.0, replacing $CaCO_3$ with different quantities of acid scavengers at high temperatures acting in the condensed phase. These formulations put in evidence the effects of the individual acid scavenger on smoke acidity and its impacts on cations and anions in the bubblers.

Table 5 gives the formulations REA01 – 10. They represent low-smoke acidity formulations with ATO as a flame retardant. They contain different acid scavengers at high temperatures acting singularly and in combination with ATH and MDH.

The ingredients of the formulations in Tables 4 and 5 were chosen because they are the typical additives found in PVC compounds for cables in the EU and compounds used in cables for fixed installation in buildings. Some of these additives are acid scavengers, flame retardants, smoke suppressants, and components of stabilizers capable of generating chlorides, potentially affecting the conductivity of the solution in the bubbling devices.

Some acid scavengers and their combinations in Table 5 are less effective than others in terms of efficiency. Two coated ground calcium carbonates, Riochim, [23] Omya hydrocarb 95 T, [24] are commonly less performant than ultrafine coated precipitated calcium carbonate, Winnofil S (PCC) [25]. AS-1B and AS-6B are potent acid scavengers at high temperatures from Reagens S.p.A. Two different synergistic mixtures are efficient at different levels: the combination of PCC and MDH are more efficient in HCl scavenging than that involving PCC and ATH. The difference in the efficiency of HCl scavenging will leave various amounts of HCl available for ATO in yielding $SbCl_3$, the leading actor that poisons the flame. [26] The aim is to see if the bubbling devices contain Sb^{3+} and if its concentration changes depending on the presence of acid scavengers with different efficiency.

The amount of ingredients is expressed per hundred resin (phr). The compounds were tested according to internal methods 4 and 5, as indicated in Tables 7 and 8.

Table 4. DINP means Di Iso Nonyl Phthalate. ESBO stands for Epoxidized Soy Bean Oil. The used antioxidant is Arenox A10, which is Pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate), CAS number 6683-19-8. COS stands for Calcium Organic Stabilizer. PCC means Precipitated Calcium Carbonate. AS-1B and AS-6B are potent acid scavengers at high temperatures.

Raw Materials	Trade name	F50.0 [phr]	F50.1 [phr]	F50.2 [phr]	F50.3 [phr]	F50.4 [phr]	F50.5 [phr]
PVC	Inovyn 271 PC	100	100	100	100	100	100
DINP	Diplast N	50	50	50	50	50	50
ESBO	Reaflex EP/6	2	2	2	2	2	2
Antioxidant	Arenox A10	0.1	0.1	0.1	0.1	0.1	0.1
COS	RPK B-CV/ 3037	3	3	3	3	3	3
$CaCO_3$	Riochim	90	0	0	0	0	0
$Al(OH)_3$	Apyral 40 CD	0	90	0	0	0	0
$Mg(OH)_2$	Ecopyren 3.5	0	0	90	0	0	0
PCC	Winnofil S	0	0	0	90	0	0
HTAS 1	AS-1B	0	0	0	0	90	0
HTAS 2	AS-6B	0	0	0	0	0	90

Table 5. DINP means Di Iso Nonyl Phthalate. ESBO stands for Epoxidized Soy Bean Oil. The used antioxidant is Arenox A10, which is Pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate), CAS number 6683-19-8. COS stands for Calcium Organic Stabilizer. PCC means Precipitated Calcium Carbonate. AS-6B is a potent acid scavenger at high temperatures. Riochim and Omya 95 T are calcium carbonates with a standard and fine particle size.

Raw Materials	Trade name	REA1 [phr]	REA2 [phr]	REA3 [phr]	REA4 [phr]	REA5 [phr]	REA6 [phr]	REA7 [phr]	REA8 [phr]	REA9 [phr]	REA10 [phr]
PVC	Inovyn 271 PC	100	100	100	100	100	100	100	100	100	100
DINP	Diplast N	50	50	50	50	50	50	50	50	50	50
ESBO	Reaflex EP/6	2	2	2	2	2	2	2	2	2	2
Antioxidant	Arenox A10	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
COS	RPK B-CV/ 3037	5	3	3	3	3	3	3	3	3	3
Antimony Trioxide	RI004	0	5	5	5	5	5	5	5	5	5
$CaCO_{3\ \text{standard}}$	Riochim	0	0	90	0	0	0	0	0	0	0
$CaCO_{3\ \text{fine}}$	Omya 95 T	0	0	0	90	0	0	0	0	0	0
PCC	Winnofil S	0	0	0	0	90	0	0	0	90	90
HTAS 2	AS-6B	0	0	0	0	0	90	0	0	0	0
$Al(OH)_3$	Apyral 40 CD	0	0	0	0	0	0	90	0	30	0
$Mg(OH)_2$	Ecopyren 3.5	0	0	0	0	0	0	0	90	0	30

Internal methods 4 and 5 use the following materials: DDW is internally produced by an ion exchange deionizer. The pH of DDW must be between 5.50 and 7.50, and conductivity must be less than 0.5 µS/mm. Buffer and conductivity standard solutions come from VWR international (pH: 2.00, 4.01, 7.00, 10.00, Conductivity: 2.0, 8.4, 14.7, 141.3 µS/mm). Dionex™ Combined Seven Anion Standard II and Dionex™ Combined Six Cation Standard-I have been used to measure the concentration of the analytes in Table 7.

2.2. Test Apparatus

Table 6 describes the utilized test apparatuses.

Table 6. Main test apparatuses utilized.

Test apparatus	Producer	model	Additional Info's
Plasticorder	Brabender	Plastograph EC	50 CC, chamber
Halogen Acid Gas test apparatus	SA Associates	Standard model	Porcelain combustion boats
Multimeter	Mettler Toledo	S213 standard kit	
Conductivity electrode	Mettler Toledo	S213 standard kit	Reference thermocouple adjusting temperature fluctuation.
pH electrode	Mettler Toledo	S213 standard kit	Reference thermocouple adjusting temperature fluctuation.
Ion Chromatography System	Thermo	Dionex IonPac™ AS22 4, x 250 mm	
Anion exchange column	Thermo	Dionex IonPac™ CS12A 4, x 250 mm	
Cation exchange column	Thermo	Aqueon	
ICP-OES	Thermo	iCAP 7000 series	

2.3. Sample Preparation

Refs 27 and 28 describe apparatuses and the procedures for preparing PVC compound test specimens in detail. In summary, the formulations in Tables 4 and 5 are mixed in a turbo mixer up to 105 °C, producing the dry blends, then processed into kneaders by plasticorder for 10 minutes. The kneaders are pressed in 0.5 mm plaques in a hydraulic press, and the test specimens for the methods indicated in Table 6 are obtained from them. Appendix A, Figures A1 and A2 give a schematic diagram of the sample preparation and testing process.

2.4. Internal methods for evaluating the species in solutions

Table 7 recalls the internal methods, measures, and determined analytes.

Table 7. Tests for acidity assessment.

Technical standard	Measurement	Temperature [°C]	Note
Internal method 4	Multimeter pH and Conductivity	Isothermal at 950 °C	DDW, pH, and Conductivity. The general method, according to the 2014 version.
	IC Anions and cations	Isothermal at 950 °C	Li^+, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, F^-, NO^{2-}, Br^-, NO^{3-}, PO_4^{3-}, SO_4^{2-}
	ICP-OES Elements	Isothermal at 950 °C	Mg, Al, Ca, Zn, Sb
Internal method 5	Multimeter pH and Conductivity	Thermal profile of EN 60754-1[1]	DDW, pH, and Conductivity. The general method, according to the 2014 version.

	IC Anions and cations	Thermal profile of EN 60754-1[1]	Li^+, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, F^-, NO^{2-}, Br^-, NO^{3-}, PO_4^{3-}, SO_4^{2-}
	ICP-OES Elements	Thermal profile of EN 60754-1[1]	Mg, Al, Ca, Zn, Sb

[1] 23-800 °C, in 40 minutes, further 20 minutes isothermal at 800 °C.

The initial procedures of internal method 4, which recall EN 60754-2, are as follows: an empty combustion boat is carried from the sample carrier into the central part of the quartz tube. The probe of a calibrated thermocouple is introduced in the central part of the quartz glass tube, and the temperature is adjusted to 950 +/- 5 °C and maintained for at least one hour. After, the solution in bubbling devices is checked to see if pH and conductivities are between 5.50 and 7.50 and be less than 0.5 µS/mm, respectively. If not, it is necessary to repeat the cleaning procedures and adopt the precautions mentioned in Part 1 of this article [27] and EN 60754-2. The tube furnace is ready for the first run when the temperature is stable. Then, a 1.000 +/- 0.001 g sample is weighed in a porcelain combustion boat. It is rapidly shifted into the quartz glass tube, moving the magnet along the sample carrier, and then the countdown starts. The fume is collected into the bubblers containing DDW for 30 min by a normalized air flux set according to the standards. After 30 minutes, the connectors are opened, and the magnet takes the combustion boat back from the quartz glass tube. The water from the bubbling devices and washing procedures is collected in a 1 L volumetric flask filled to the mark. All precautions mentioned in Part I of this article [27] should be taken to prevent errors leading to poor repeatability and reproducibility. Therefore, the smoke acidity measurements should be repeated more times for each sample, and a statistical method for analyzing the measurements should be adopted.

The initial procedures of internal method 5 are as follows: the thermal profile of EN 60754-1 has been applied: 40 +/-5 minutes to 800°C and 800°C +/-10°C for a further 20+/-1 minutes. The calibrated thermocouple and the countdown are used to precisely check the heating regime in terms of time and temperature. This test is run by processing an empty combustion boat and checking the water quality in bubbling devices, stating the cleaning status of the test apparatus.

The detection procedures of the above-indicated methods are the following. Internal methods 4 and 5 utilize the multimeter and electrodes for measuring pH and conductivity. The general method in EN 60754-2:2014[1] was applied to analyze the precision of pH and conductivity data. It requires the measurement of the coefficient of variation (CV) of pH and conductivity, which implies three or more replicates for each sample.

Internal methods 4 and 5 also analyze the anions, including chlorine, bromine, and fluorine, through the IC anion exchange column (Table 6). They also detect the cations indicated through IC (cation exchange column, Table 6) and ICP-OES. The ISO 10304-1 framework performed IC for detecting seven anions. Without a pre-treatment of the sample, the standard has the following lower application limits: ≥ 0.05 mg/L for bromine and nitrite and ≥ 0.1 mg/L for chlorine, fluorine, nitrate, orthophosphate, and sulfate. The framework of ISO 14911 [29] was used for determining the cation concentration. The lower limits of application are the following: lithium ≥ 0.01 mg/L, sodium, ammonium, and potassium ≥ 0.1 mg/L, and magnesium and calcium ≥ 0.5 mg/L. ISO 10304-1 and ISO 14911 are designed to detect analytes below 10 mg/g, and therefore, we modified some of their procedures for dosing anions and cations at concentrations up to 200 mg/g. For the methods requiring IC measurements, the rules reported in paragraph 8 of IEC 60754-3:2011 have been adopted to evaluate the data's precision: two measurements with a difference of less than 0.1 mg/g and the ratio between the mean and standard deviation of less than 0.25. ICP-OES has been performed according to ISO 11885 [30] to complete the elemental analysis focusing on those elements (not detected by IC) capable of reaching the bubbling devices through evaporation of the molecules containing them, coming from the stabilizer and flame retardant, usually in the PVC compounds: Sb from antimony

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[1] EN 60754-2/A1:2020 [2] has a new way to evaluate the data not considered in this paper.

trioxide, and Zn and Al from the stabilizer and flame-retardant fillers. The limits of quantification (LOQ) at the specific used wavelength are the following: antimony and calcium ≥ 0.1 mg/L, zinc and magnesium ≥ 0.0033 mg/L, and aluminum ≥ 0.001 mg/L.

Performing internal methods 4 and 5, the first aliquots of the solution from bubbling devices are collected into polypropylene flasks and utilized for pH and conductivity measures. pH and conductivity are taken at 25°C +/- 1. Before each measurement, pH is calibrated at two points (4.01 and 7.00), and conductivity at 1 point at 141.3 µS/mm. The measured values are corrected by the correction standard closer to them. The second aliquots are used to detect anions and cations through IC. Iodine content has not been measured because its presence in PVC compounds is not expected. After all, no additive can be a potential source. The third aliquots are utilized for ICP-OES measurements. Appendix A, Figures A1 and A2 give a schematic diagram of the sample preparation and testing process.

3. Results

Table 8 shows the pH and conductivity of the formulations in Table 4, performing internal method 4. The tested formulations are the same as in Ref. 28. Data were collected in a second trial run to have fresh electrolyte solutions available for IC and ICP. In fact, stored solutions have a shelf life of a few days, even if polypropylene flasks are utilized. However, pH and conductivities are consistent with those reported in Ref. 28. Precisely, the data of the second run trials are in 5.0 % of the CV of the data of the first trials. The calculated conductivity from pH utilizing the DHO equation in Annex B is shown together with the precision of experimental measurements, quantified as the percentage error relative to the theoretical DHO conductivity.

Table 8. pH and Conductivity of the compounds in Table 4 are shown performing internal method 4 (isothermal at 950 °C). The table also reports the pH and Conductivity of the first run performed in Ref. 28. The thermal profile of EN 60754-2 has been used. The mean values, coefficient of variation, and standard deviations are reported. The calculated conductivity utilizing the DHO equation is presented together with the precision of experimental measurements, quantified as the percentage error relative to the theoretical DHO conductivity.

Formulation →	**F50.0**	**F50.1**	**F50.2**	**F50.3**	**F50.4**	**F50.5**
pH	2.668	2.291	2.291	2.715	2.748	2.810
SD_{pH}	0.090	0.112	0.095	0.030	0.125	0.122
CV_{pH} [%]	3.4	4.9	4.1	1.1	4.5	4.3
Conductivity [mS/mm]	95.9	223.2	222.7	77.0	72.1	73.2
SD_c	3.2	8.8	10.2	4.2	3.2	3.1
CV_c [%]	3.3	3.9	4.6	5.5	4.4	4.2
Accuracy [%] from DHO model	5.7	5.1	4.8	-5.6	-4.9	11.1
pH (1st run)	2.62	2.27	2.27	2.74	2.89	2.79
Conductivity [mS/mm] (1st run) [16]	97.3	221.5	224.3	74	70.1	70.1
Conductivity [mS/mm] (DHO)	90.7	212.4	212.4	81.6	75.8	65.9

Table 9 reports pH and [Cl$^-$] measured applying internal method 4: precisely measured pH is in Column 2, the [H$^+$] calculated from pH in Column 3, and the [Cl$^-$] derived from HCl in Column 6. Column 7 gives the [Cl$^-$] from IC measurements.

Table 9. Chlorine concentrations from bubblers are reported for the formulation of Table 4. Internal method 4 was used. In column 6, chlorine has been calculated for pH values, assuming HCl is the only source of it. Column 7 shows the chlorine concentrations from IC.

Sample	pH	$[H^+]$ Mol/L	$[Cl^-]$ Mol/L	$[Cl^-]$ g/L	$[Cl^-]$ mg/L	$[Cl^-]$ IC [mg/L]	Delta
F50.0	2.668	0.0021503	0.0021503	0.0762348	76.2	78.7	-3.26
F50.1	2.291	0.0051227	0.0051227	0.1816155	181.6	177.0	2.54
F50.2	2.291	0.0051227	0.0051227	0.1816155	181.6	175.8	3.21
F50.3	2.715	0.0019297	0.0019297	0.0684153	68.4	69.1	-1.02
F50.4	2.748	0.0017865	0.0017865	0.0633363	63.3	64.6	-2.04
F50.5	2.810	0.0015506	0.0015506	0.0549734	55.0	57.0	-3.67

Tables 10 and 11 show anions and cations concentrations found in the solutions performing internal method 4 on the formulations in Table 4. Table 12 shows the Al, Zn, and Sb concentrations measured through ICP-OES.

Table 10. IC measured the anions concentration of the first set of formulations. Internal method 4 was performed in isothermal at 950 °C. LOQ according to ISO 10304-1: Br^- and NO^{2-} ≥ 0.05 mg/L; Cl^-, F^-, NO^{3-}, PO_4^{3-} and SO_4^{2-} ≥ 0.1 mg/L.

Sample	$[Cl^-]$ mg/L	SD $[Cl^-]$ mg/L	$[F^-]$ mg/L	$[NO^{2-}]$ mg/L	$[Br^-]$ mg/L	$[NO^{3-}]$ mg/L	$[PO_4^{3-}]$ mg/L	$[SO_4^{2-}]$ mg/L
F50.0	78.72	2.91	0.10	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
F50.1	177.00	5.50	0.11	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
F50.2	175.78	6.76	0.11	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
F50.3	69.11	2.44	0.11	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
F50.4	64.63	2.50	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
F50.5	56.99	1.89	0.10	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ

Table 11. IC measured the cations concentration of formulations in Table 4. Internal method 4 was performed in isothermal at 950 °C. LOQ according to ISO 14911: Li^+ ≥ 0.01 mg/L; Na^+, NH_4^+ and K^+ ≥ 0.1 mg/L; Mg^{2+} and Ca^{2+} ≥ 0.5 mg/L.

Sample	$[Li^+]$ mg/L	$[Na^+]$ mg/L	$[NH_4^+]$ mg/L	$[K^+]$ mg/L	$[Mg^{2+}]$ mg/L	$[Ca^{2+}]$ mg/L
F50.0	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
F50.1	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
F50.2	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
F50.3	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
F50.4	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
F50.5	0.01	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ

Table 12. ICP-OES measured the cations concentration of the formulation in Table 4. Internal method 4 was performed, and isothermal at 950 °C was used. LOQ according to ISO 11885: Sb ≥ 0.1 mg/L, Zn ≥ 0.0033 mg/L, and Al ≥ 0.001 mg/L.

Sample	[Al] mg/L	[Sb] mg/L	[Zn] mg/L
F50.0	< LOQ	< LOQ	< LOQ
F50.1	< LOQ	< LOQ	< LOQ

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F50.2	< LOQ	< LOQ	< LOQ
F50.3	< LOQ	< LOQ	< LOQ
F50.4	< LOQ	< LOQ	< LOQ
F50.5	< LOQ	< LOQ	< LOQ

Table 13 displays the compounds' pH and conductivity in Table 4, performing internal method 5. As the data in Table 8 shows, pH and conductivity values from Ref. 28 are also reported. The conductivity determined through pH using the DHO equation in Annex B is presented alongside the accuracy of experimental measurements, expressed as the percentage deviation compared to the theoretical DHO conductivity.

Table 13. pH and Conductivity of the compounds in Table 4 are shown, performing internal method 5 (40 minutes at 800 °C and further 20 min at 800 °C). The table also reports the pH and Conductivity of the first run. [28] The mean values, coefficient of variation, and standard deviations are reported. The calculated Conductivity utilizing the DHO equation is presented with the precision of experimental measurements, quantified as the percentage error relative to the theoretical DHO conductivity.

Formulation →	**F50.0**	**F50.1**	**F50.2**	**F50.3**	**F50.4**	**F50.5**
pH	2.515	2.293	2.380	3.198	3.556	3.273
SD_{pH}	0.100	0.110	0.080	0.081	0.087	0.102
CV_{pH} [%]	4.0	4.8	3.4	2.5	2.4	3.1
Conductivity [mS/mm]	135.7	219.7	174.2	30.7	11.6	24.9
SD_c	6.3	5.4	8.7	2.5	0.2	1.2
CV_c [%]	4.6	2.5	5.0	8.1	1.7	4.8
Accuracy [%] from DHO model	5.9	3.9	0.2	11.6	-4.9	7.3
pH (1st run)	2.63	2.3	2.29	3.26	3.52	3.2
Conductivity [mS/mm] (1st run) [16]	100.4	206.4	208.9	23.7	13.5	25.7
Conductivity [mS/mm] (DHO)	128.1	211.4	173.8	27.5	12.2	23.2

Table 14 reports pH (multimeter) and $[Cl^-]$ through IC, measured applying internal method 5 on the formulations in Table 4. It shows pH (Column 2), the $[H^+]$ calculated from pH (Column 3), and the $[Cl^-]$ derived from HCl (Column 6). Column 7 gives the $[Cl^-]$ from IC measurements.

Table 14. Chlorine concentrations from bubblers are reported for the formulations in Table 4. Internal method 5 was used. In column 6, chlorine has been calculated for pH values, assuming HCl is the only source of it. Column 7 shows the chlorine concentrations from IC.

Sample	**pH**	**$[H^+]$ Mol/L**	**$[Cl^-]$ Mol/L**	**$[Cl^-]$ g/L**	**$[Cl^-]$ mg/L**	**$[Cl^-]$ IC [mg/L]**	**Delta**
F50.0	2.515	0.0030584	0.0030584	0.1084309	108.43	113.82	-4.97
F50.1	2.293	0.0050933	0.0050933	0.1805731	180.57	176.10	2.47
F50.2	2.380	0.0041687	0.0041687	0.1477927	147.79	147.25	0.37
F50.3	3.198	0.0006339	0.0006339	0.0224726	22.47	21.23	5.55
F50.4	3.556	0.0002780	0.0002780	0.0098549	9.85	7.42	24.67
F50.5	3.273	0.0005339	0.0005339	0.0189301	18.93	17.41	8.03

Tables 15 and 16 show anions and cations concentration in the solutions performing internal method 5. Table 17 shows the Al, Zn, and Sb concentrations measured through ICP-OES.

Table 15. IC measured the anions concentration of the first set of formulations. Internal method 5 was performed, and the thermal profile of EN 60754-1 was applied. LOQ according to ISO 10304-1: Br^- and NO^{2-} ≥ 0.05 mg/L; Cl^-, F^-, NO^{3-}, PO_4^{3-} and SO_4^{2-} ≥ 0.1 mg/L.

Sample	[Cl^-] mg/L	SD [Cl^-]	[F^-] mg/L	[NO^{2-}] mg/L	[Br^-] mg/L	[NO^{3-}] mg/L	[PO_4^{3-}] mg/L	[SO_4^{2-}] mg/L
F50.0	113.82	2.32	0.10	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
F50.1	176.10	4.23	0.11	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
F50.2	147.25	2.66	0.11	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
F50.3	21.23	1.21	0.11	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
F50.4	7.42	0.57	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
F50.5	17.41	1.00	0.10	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ

Table 16. IC has measured the cations concentration of the first set of formulations. Internal method 5 was performed, and EN 60754-1 thermal profile was used. LOQ according to ISO 14911: Li^+ ≥ 0.01 mg/L; Na^+, NH_4^+ and K^+ ≥ 0.1 mg/L; Mg^{2+} and Ca^{2+} ≥ 0.5 mg/L.

Sample	[Li^+] mg/L	[Na^+] mg/L	[NH_4^+] mg/L	[K^+] mg/L	[Mg^{2+}] mg/L	[Ca^{2+}] mg/L
F50.0	0.01	0.10	< LOQ	0.10	< LOQ	< LOQ
F50.1	< LOQ	0.10	0.12	0.10	< LOQ	< LOQ
F50.2	< LOQ	0.10	0.19	< LOQ	< LOQ	< LOQ
F50.3	0.01	0.13	< LOQ	0.19	< LOQ	< LOQ
F50.4	0.01	0.10	< LOQ	0.19	< LOQ	< LOQ
F50.5	0.01	0.17	< LOQ	0.33	< LOQ	< LOQ

Table 17. ICP-OES measured the cations concentration of the formulation in Table 1. Internal method 5 was performed, and EN 60754-1 thermal profile was used. LOQ ISO 11885: Sb ≥ 0.1 mg/L, Zn ≥ 0.0033 mg/L, and Al ≥ 0.001 mg/L.

Sample	[Al] mg/L	[Sb] mg/L	[Zn] mg/L
F50.0	< LOQ	< LOQ	< LOQ
F50.1	< LOQ	< LOQ	< LOQ
F50.2	< LOQ	< LOQ	< LOQ
F50.3	< LOQ	< LOQ	< LOQ
F50.4	< LOQ	< LOQ	< LOQ
F50.5	< LOQ	< LOQ	< LOQ

Tables 18 and 19 display the results of internal methods 4 and 5, specifically IC through anion column exchange. Tables 20 and 21 show the ICP-OES results.

Table 18. IC measured the anions concentration of the formulations in Table 5. Internal method 4 was performed, and EN 60754-2 thermal profile was applied. LOQ: Br^- and NO^{2-} ≥ 0.05 mg/L; Cl^-, F^-, NO^{3-}, PO_4^{3-} and SO_4^{2-} ≥ 0.1 mg/L.

Sample	[Cl^-] mg/L	SD [Cl-]	[F^-] mg/L	[NO^{2-}] mg/L	[Br^-] mg/L	[NO^{3-}] mg/L	[PO_4^{3-}] mg/L	[SO_4^{2-}] mg/L
REA3	98.70	1.18	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ

REA4	70.94	1.20	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
REA5	97.07	2.78	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
REA6	64.05	1.30	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
REA7	206.06	6.23	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
REA8	197.12	8.23	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
REA9	42.81	2.41	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
REA10	62.05	1.23	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ

Table 19. IC measured the anions concentration of the formulations in Table 5. Internal method 5 was performed, and EN 60754-1 thermal profile was applied. LOQ: Br^- and NO^{2-} ≥ 0.05 mg/L; Cl^-, F^-, NO^{3-}, PO_4^{3-} and SO_4^{2-} ≥ 0.1 mg/L.

Sample	**[Cl⁻] mg/L**	**SD [Cl-]**	**$[F^-]$ mg/L**	**$[NO^{2-}]$ mg/L**	**$[Br^-]$ mg/L**	**$[NO^{3-}]$ mg/L**	**$[PO_4^{3-}]$ mg/L**	**$[SO_4^{2-}]$ mg/L**
REA3	64.47	1.93	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
REA4	60.81	2.43	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
REA5	23.44	1.23	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
REA6	2.98	0.45	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
REA7	173.64	2.45	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
REA8	192.44	3.25	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
REA9	10.33	1.00	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
REA10	25.00	1.25	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ

Table 20. ICP-OES measured the cations concentration of the formulations in Table 5. Internal method 4 was performed, and the thermal profile of EN 60754-2 was used. LOQ: Sb and Ca ≥ 0.1 mg/L, Zn and Mg ≥ 0.0033 mg/L, and Al ≥ 0.001.

Sample	**[Ca] mg/L**	**[Mg] mg/L**	**[Al] mg/L**	**[Sb] mg/L**	**[Zn] mg/L**
REA3	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
REA4	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
REA5	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
REA6	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
REA7	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
REA8	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
REA9	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ
REA10	< LOQ	< LOQ	< LOQ	< LOQ	< LOQ

Table 21. ICP-OES measured the cations concentration of the formulations in Table 5. Internal method 5 was performed, and EN 60754-1 thermal profile was used. LOQ: Sb and Ca ≥ 0.1 mg/L, Zn and Mg ≥ 0.0033 mg/L, and Al ≥ 0.001.

Sample	**[Al] mg/L**	**[Sb] mg/L**	**[Zn] mg/L**
REA3	< LOQ	< LOQ	< LOQ
REA4	< LOQ	< LOQ	< LOQ
REA5	< LOQ	< LOQ	< LOQ
REA6	< LOQ	< LOQ	< LOQ
REA7	< LOQ	< LOQ	< LOQ
REA8	< LOQ	< LOQ	< LOQ
REA9	< LOQ	< LOQ	< LOQ

REA10	< LOQ	< LOQ	< LOQ

Table 22. pH and Conductivity measured from cables from the market. FG16OR16, where G16 is HEPR, R16 is a flame retarded PVC jacket, S18 and R18 are respectively a PVC insulation and jacket from FS18R18 cable, and S17 is a single wire insulation from FS17 cable. FG16OR16, FG18R18, and FS17 are Italian non-harmonized cables. Plenum compound is a flame retarded compound developed to meet the requirement of the US standard of NPA 0262. TPU-FR is a flame retarded jacket made up of PU polyether based with melamine in the intumescent system.

Formulation →	**R16**	**S18**	**R18**	**S17**	**PVC Plenum**	**TPU-FR**
pH	2.673	2.396	2.651	2.361	2.38	8.20
SD_{pH}	0.132	0.114	0.1024	0.09	0.115	0.22
CV_{pH} [%]	4.9	4.8	3.9	3.8	4.8	2.7
Conductivity [mS/mm]	88.4	171.9	94.3	189	243.4	32.2
SD_c	1.2	5.4	4.2	9.0	10.0	1.3
CV_c [%]	1.4	3.1	4.5	4.8	4.1	4.0
Conductivity [mS/mm] (DHO)	89.7	167.6	92.3	181.3	173.8	n.a.
Accuracy [%]	-1.45	2.57	2.17	4.25	40.0	n.a.

4. Discussion

4.1. Species Found in Solutions

Formulations F50.0 – F50.5 in Table 4 do not have ATO, and F50.3, F50.4, and F50.5 contain acid scavengers at high temperatures acting in the condensed phase. F50.1 and F50.2, having respectively ATH and MDH as not efficient acid scavengers, give the highest acidity at 950°C (Table 8, pH and conductivity). F50.0 with GCC reaches 2.67 pH, and F50.3-5 with the performant acid scavengers are slightly better than F50.0, which means that at high temperatures, even the excellent acid scavengers (Winnofil S, AS-1B, and AS-6B) suffer the fast kinetic of HCl evolution from zip elimination. Table 9 reports the chlorine concentration in mg/L in column 7 from IC measurements and the comparison with [Cl^-] (column 6) derived from pH measurements in Table 8, assuming a complete dissociation of HCl and the absence of other acidic species in the bubblers from side reactions during the combustions. The delta in column 8 indicates clearly that both measurements are comparable. That can be explained from the data in Table 10, where only Cl^- is detected, and HCl is acidity's driving force. The formulation in Table 5 has no bromine, nitrate, nitrite, orthophosphate, or sulfate source. The only potential sources could be bromine and orthophosphate from brominated or phosphorous containing compounds used as flame retardants not used in this research.

Table 11 reports the concentration of 6 cations found in the bubbling devices. The possible candidates, chloride formed through the reaction between some ingredients in the stabilizer one pack and fillers and flame retardant fillers, are mainly $ZnCl_2$, $CaCl_2$, and $MgCl_2$. $ZnCl_2$ in formulation F50.0 – 5 is only yielded from the reaction between calcium organic stabilizer (COS), actually a calcium zinc stabilizer, and HCl. The quantity of Zn in all compounds is enough to be seen in the solution in case of evaporation and, therefore, potentially higher than the LOQ of ISO 11885. $ZnCl_2$ can also derive from zinc salts commonly found in some flame retardant packages not used in those compounds. It is a soluble salt having a boiling temperature of around 720°C. Therefore, it could evaporate and reach the bubblers, affecting conductivity. The data in Table 11 confirm the absence of Zn^{2+} in the solution, probably because $ZnCl_2$ hydrolyzes, yielding ZnO and HCl. The $CaCl_2$ derives from the reaction between HCl and $CaCO_3$ and calcium stearate and $Ca(OH)_2$ in the stabilizer one pack. Obviously, it remains in the condensed phase without evaporation, which occurs massively around the boiling point over 1900 °C. However, it can also hydrolyze over 900 °C, leaving CaO in the ashes and releasing HCl in the gas phase. $MgCl_2$, which has a boiling point of around 1600 °C, comes from MDH. It is prone to be hydrolyzed between 450 °C and 550°C, leaving MgO and HCl. [31,32] ATH does not react at all with HCl (which explains the scarce HCl scavenging efficiency of formulation F50.2). Therefore, Zn, Al, Ca, and Mg ions are absent in the bubbling devices, indicating that in formulations F50.0-F50.5, the conductivity is massively affected by HCl only.

The formulations REA01-10 follow the behavior of F50.0-5, confirming that Sb is not found in the solution. That is because $SbCl_3$ reaching the bubblers gives the following reaction:

$$SbCl_3 + H_2O \rightarrow SbOCl + 2HCl \quad (1)$$

where SbOCl, insoluble in water, makes Sb not accessible for ICP-OES after filtering procedures, but in any case, not available as a free ion capable of affecting the conductivity.

The exploration applying a ramp through method 5 (Tables 14-17, 21) shows the same trends. HCl drives pH and conductivity. The only difference between the two sets is in the concentration of HCl in solutions of formulations containing potent acid scavengers, releasing less HCl in the bubblers when the heating conditions are milder (ramp of 20°C/min) and at a lower temperature (800 °C vs. 950°C).

4.2. Statistical Approach

Assuming an HCl scavenging mechanism in the condensed phase and negligible the contribution of the evaporation of some chlorides in the gas phase, HCl itself is the primary driver of the acidity and conductivity and, therefore, the correlation model between conductivity and pH should follow Equation A1 in Annex B, according to the DHO theory (DHO model). Annex B explains in detail the DHO model, and Annex C the conductivity and pH values for the ideal solutions of HCl following the DHO model. The theoretical values predicted by the DHO model are presented in Tables 8, 13, and 22, juxtaposed with experimental ones and their accuracy as a metric for the deviation from the model. Examination of the data in Tables 8 and 13 and Figure 1 reveals that the accuracy of the conductivity of the investigated formulations remains below 12% in all instances, closely aligning with the predicted by the DHO model.

Building upon the considerations outlined in Section 4.1, Tables 8 and 13 and Figure 1 highlight formulations characterized by evident HCl scavenging in the condensed phase, with no discernible chloride evaporation, in which HCl is the driving force of the acidity and conductivity. Additionally, with no information on their constituents, PVC jackets and insulations from the market exhibit analogous behavior (Table 22 and Figure 2). This observation strongly suggests a condensed-phase mechanism that aligns well with the values predicted by the DHO model. An exception is noted in the plenum compound, demonstrating a deviation of approximately 40%. This anomaly can be rationalized by ammonium octa molybdate (AOM), which liberates ammonia at around 270 °C. The ensuing reaction with HCl introduces an airborne NH_4Cl into the bubblers, exerting a pronounced influence on both pH and conductivity synchronously. In conclusion, the measure of the accuracy as a metric for the deviation from the DHO model can be a valid and rapid screening which can be done with pH and conductivity measurements in order to understand if the HCl is the driver of the acidity, the mechanism acts in the condensed phase and if there are the interference of chlorides or other substances evaporating during the combustion.

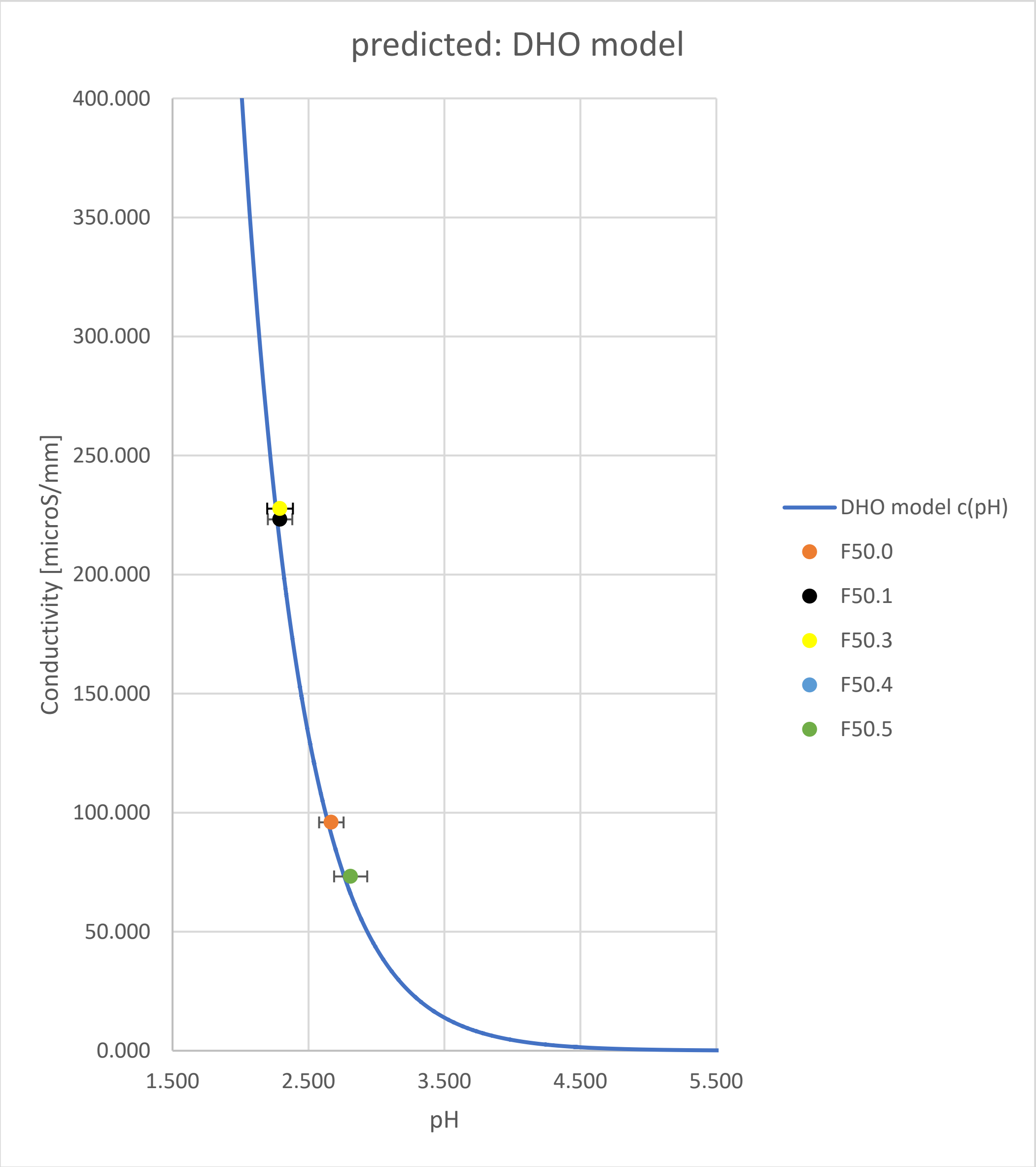

Figure 1. DHO model (blue line) and experimental values from F50.0-F50.5 a according to method 4 at 950 °C.

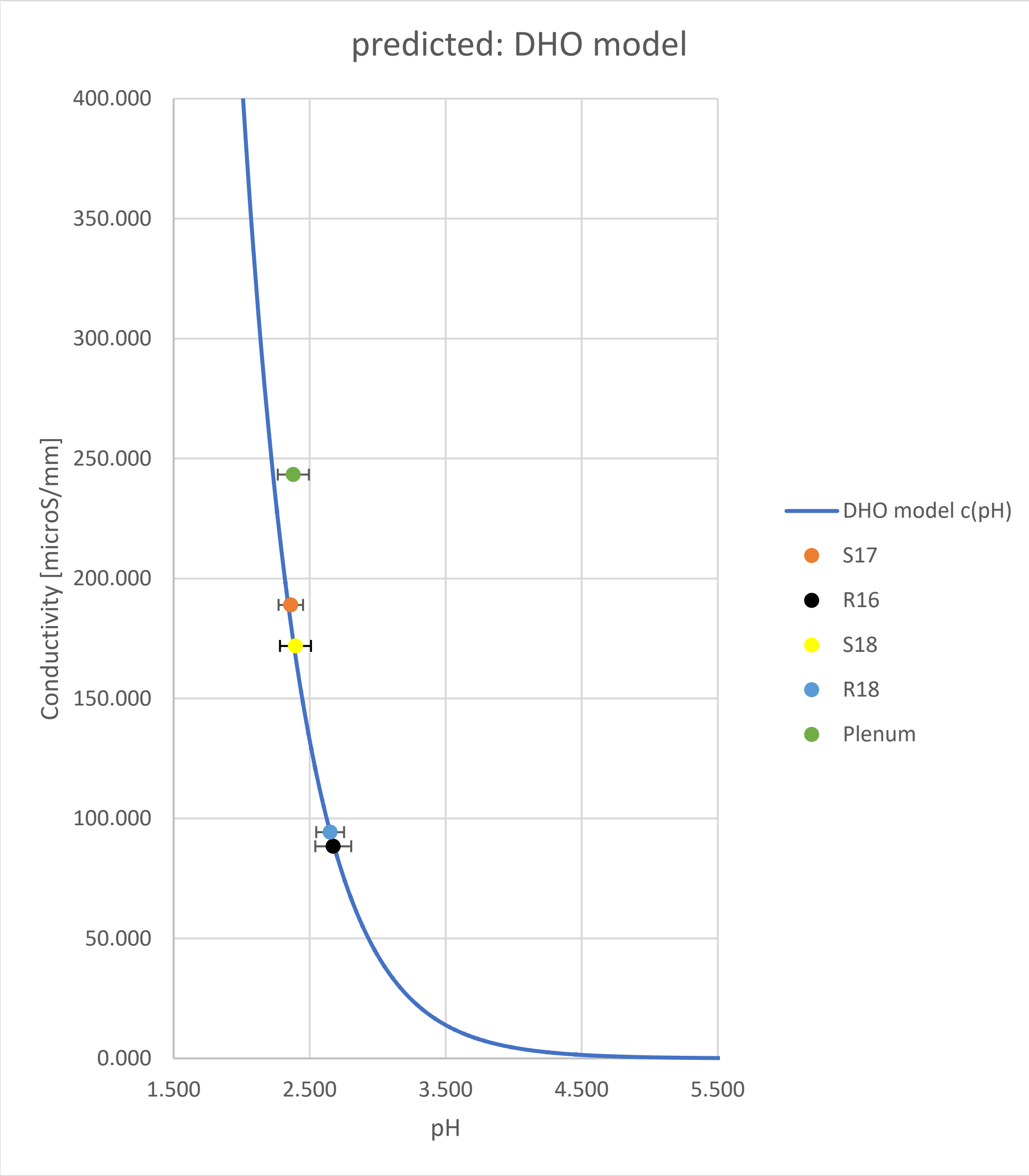

Figure 2. DHO model (blue line) and experimental values form S17, R16, S18, R18, and plenum compound tested according to method 4 at 950 °C.

4.3. The Idiosyncrasy of EN 60754-2, EN 50525-1 and EN 50620

Other polymer compounds with different thermal degradation patterns show different correlations between pH and conductivity. A typical example of this is the measurement of flame retarded TPU polyether, which shows pH 8.20 and conductivity 32.2 µS/mm. (Table 22) A cable made with this compound would bring a classification a_3. Measurements revealed the effect of ammonia evolving from melamine, effectively becoming a gas-phase acid scavenger and affecting pH but also conductivity pushed over the limit of 10 µS/mm for the class a_2. That is a bizarre case where such a cable would be in class a_3 (the worst case for acidity), not halogen free according to the halogen assessment of annex B of EN 50525-1. That also explains the derogation introduced in EN 50620, where the conductivity limit was enhanced to 40 µS/mm as the best compromise between conductivity and flame retardancy.

5. Conclusions

Many standards based on tube furnaces are available to assess indirectly and/or quantify HCl released during the combustion. The paper reviews in the first part, highlighting their current status, where they are used, what they determine, their weaknesses, and the flawless. Specifically, EN 60754-2 has been adopted by CPR to identify the additional classification for acidity through pH and conductivity measurements. The flawness of the standard in assessing acidity has been explained elsewhere [33], mainly related to the final temperature of the test, which affects the capability of the acid scavenger to trap HCl efficiently. [28,33,34] However, using that standard can generate other complicated confusion. Halogen-free jackets containing melamine-based intumescent systems as flame retardants can bring a pH of more than 4.3 with a conductivity of more than 10 µS/mm. Such values would bring the cable out of the halogen-free group according to annex B of EN 50525-1 and in the worst case of acidity according to EN 60754-2, EN 15301-6, and EN 50575 despite the emission of basic fumes. The impossibility of finding a good flame retardance with a conductivity of less than 10 µS/mm forced the limit in EN 50620 up to 40 µS/mm. All this shows how it is needed to review the concept of halogen-free assessment in EN 50525-1 and the additional classification for acidity in CPR, and in this, IEC EN 60754-3 will probably play a crucial role.

The experimental part of the paper shows how the evaluation of the species in solution affecting acidity and conductivity plays a critical role in designing the proper HCl scavenger to be used in PVC cable compounds for meeting the best classifications. Standard PVC compounds for cables used in CPR contain mainly MDH, ATH, and ATO as flame retardants and always calcium zinc as a stabilizer. IC and ICP-OES were used in this paper to see the main actors driving acidity and the conductivity of the solution in the bubblers. In the process of combustion of CPR compounds for cables performing a ramp to 800°C or in isothermal at 950°C, it has been shown that chlorine is the dominant species in the solutions, and no evaporation of substances capable of generating electrolytes occurs. In this way, the solution in the bubblers behaves as a standard solution of HCl following the DHO equation for HCl. Plenum PVC compounds containing AOM behave differently. Here, AOM decomposes at 270°C, releasing ammonia and generating NH_4Cl, reaching the bubblers with HCl and bringing more electrolytes, further increasing the solution's conductivity. The deviation from the DHO model here is high (more than 40%) as a clear indication of the scavenging in the gas phase of HCl and the yielding of products capable of severely affecting the conductivity of the solutions in the bubblers. Therefore, a simple measure of pH and conductivity and the deviation of DHO can be used as a fast screening, taking into account the evaporation of chlorides or the formation of acidic, basic, or neutral species in the gas phase capable of affecting pH and conductivity with a different magnitude as HCl does.

Finally, the paper showed how IC is a potent detection method to verify what species actually affect pH and conductivity. This exploration can be done to quantify halogen species and other anions or cations dissolved in the solutions coming from the PVC compound combustion. The quantification of $[Cl^-]$ through IC aligns with the [Cl-] derived from pH measurements, assuming all H comes from the totally dissociated HCl. Furthermore, it has been shown that IC can be easily performed at the low concentrations indicated in the IEC EN 60754-3 and even at higher concentrations, making the standard a valid substitute for EN 60754-2 and EN 60754-1.

Supplementary Materials: The following are available online at www.mdpi.com/xxx/s1, Table S1: commercial additives.

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Abbreviations

PVC—Poly(vinyl chloride);
EU—European Union;
CPR—Construction Product Regulation;
DDW—Double Deionized Water;
LOQ – Limit of Quantification;
HCl—Hydrogen chloride;
GPP – General Purpose Plasticizer;
ATO – Antimony Trioxide;
ATH – Aluminum Tri Hydroxide;
MDH – Magnesium Di Hydroxide;
PCC—Precipitated Calcium Carbonate;
GCC—Ground Calcium Carbonate;
Phr—Part per Hundred Resin;
DINP—Di Iso Nonyl Phthalate;
ESBO—Epoxidized Soy Bean Oil;
COS—Calcium Organic Stabilizer;
IC – Ion Chromatography;
ICP-OES — Inductively Coupled Plasma – Optical Emission Spectroscopy;
SD—Standard Deviation;
CV—Coefficient of variation;
DHO – Debye-Hückel-Onsager;
AOM – Ammonium Octa Molybdate.

Appendix-A. A schematic diagram of the sample preparation and testing process

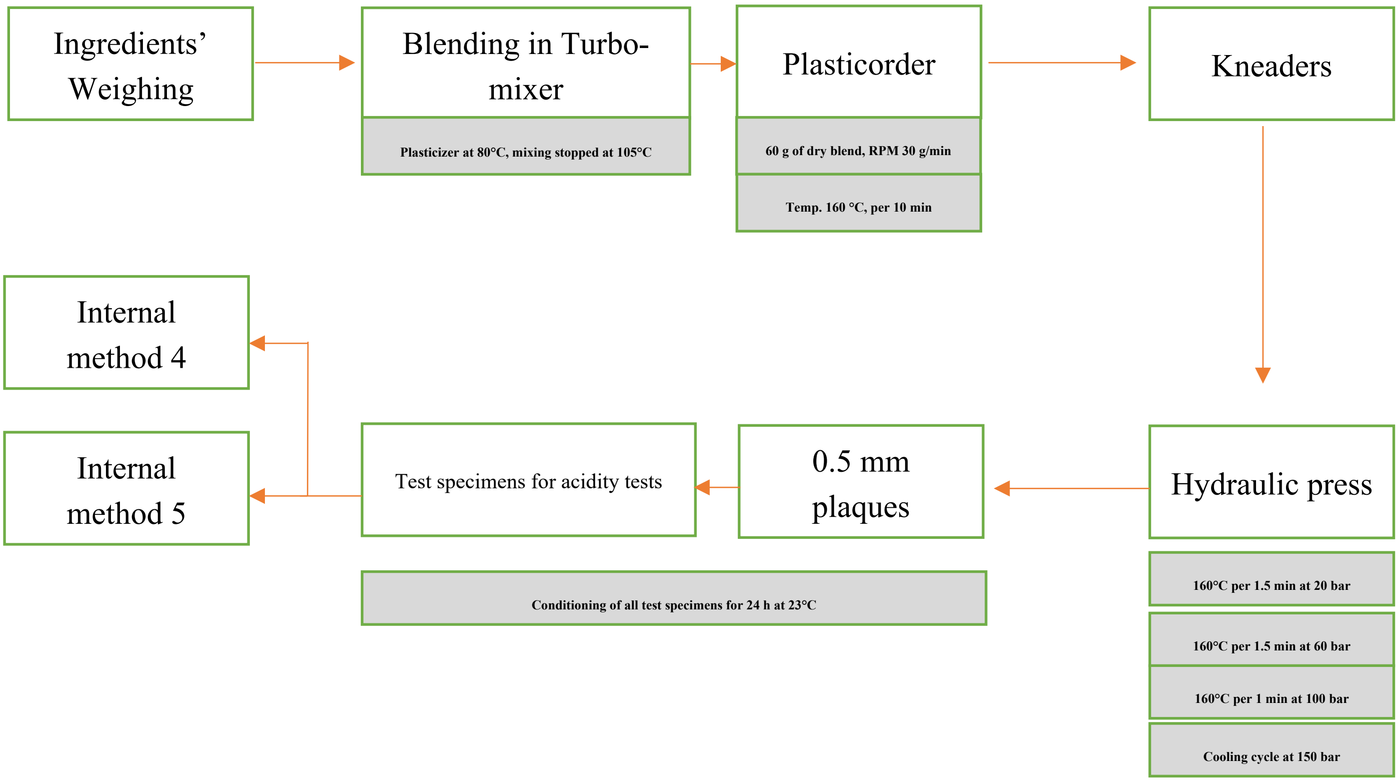

Figure A1. A schematic diagram of the sample preparation.

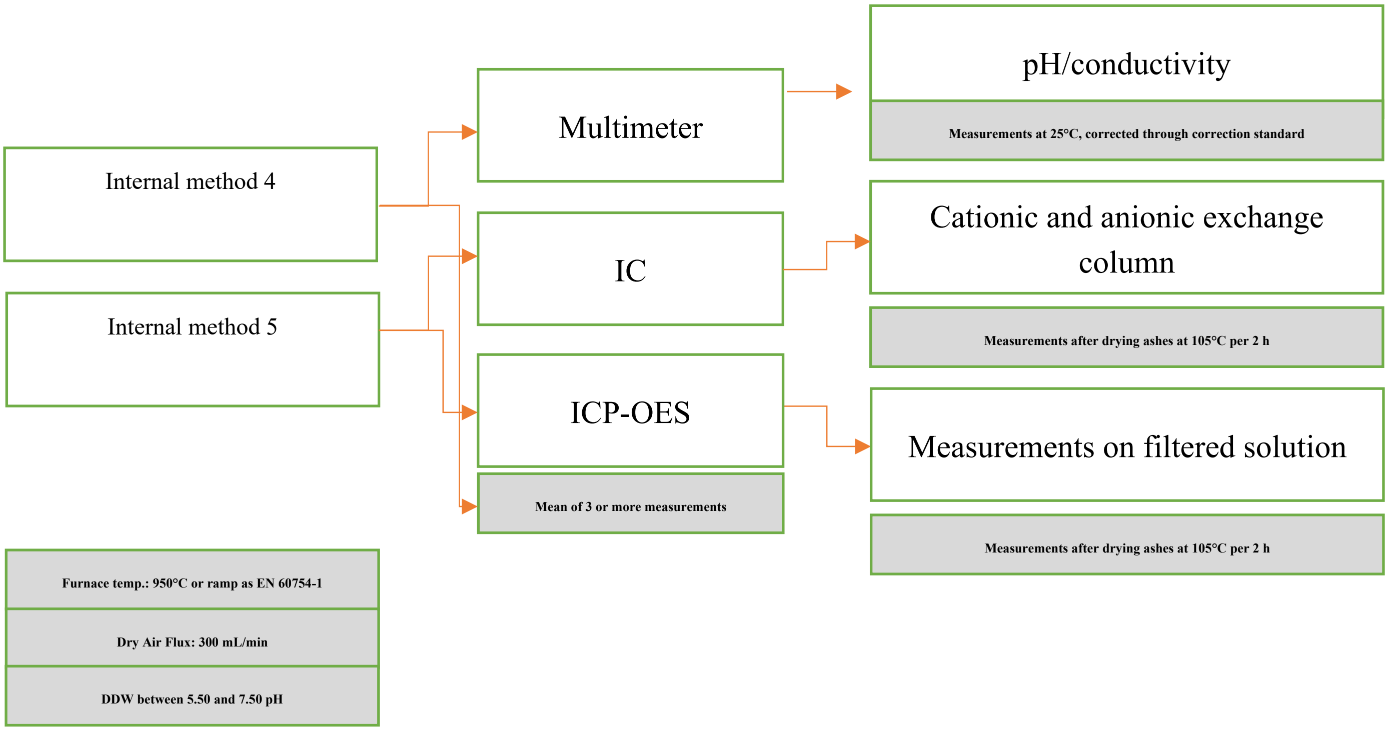

Figure A2. A schematic diagram of the testing process and main conditions.

Appendix-B. Statistical approach: the mathematical relationship between C and pH for standard solutions of HCl

The empirical investigation of the pH-conductivity relationship in HCl solutions involves systematically varying HCl concentrations and employing statistical algorithms to determine the optimal equation, denoted as C(pH), that best models the observed data. Equation A1 with coefficients **a** and **b** were obtained through the XLSTAT program and shows the nonlinear regression of data of the conductivity, **C**, as a function of **pH**, obtained from standard solutions of HCl with a pH ranging between 2.00 up to 6.88.

$$C = \boldsymbol{a}\, e^{(-\boldsymbol{b}\, pH)} \quad \text{(A1)}$$

where **a** = 40476.18 and **b** = 2.2897

The research on smoke acidity compounds since 2013 produced lots of data on pH and conductivity, performing EN 60754-2 at 950°C, of many samples made of PVC insulation, bedding, and jacket formulations. The plotting of data of 1002 measurements of pH and conductivity gave the equation A2,

$$C = \boldsymbol{a}\, e^{(-\boldsymbol{b}\, pH)} \quad \text{(A2)}$$

where **a** = 39352.80 and **b** = 2.27356

Another approach that permits a mathematical relationship between pH and conductivity can be derived from the DHO theory. For a solution where molar concentration, **c**, is less than 0.001 mol/L, the molar conductivity for any electrolyte can be roughly calculated using the DHO equation, valid for a symmetrical and equal charge 1 cation and anion. [35] The equation is the following A3:

$$\Lambda_{\mathrm{m}} = \Lambda_{\mathrm{m}}^{0} - (\mathbf{A} + \mathbf{B}\Lambda_{\mathrm{m}}^{0})c^{0.5} \quad \text{(A3)}$$

where Λ_{m}^{0} is the molar conductivity at infinite dilution, **A**= 60.20 cm^2 $dm^{3/2}$/ $mol^{3/2}$ and **B** = 0.229 $dm^{3/2}$/$mol^{1/2}$ at 25 °C. [36]

With a higher concentration than 0.001 mol/L, eh face consistent deviation from the DHO equation due to the solution's interaction between anion and cations. The detailed theory is explained elsewhere. [35]

From Kohlrausch's law, the electrical conductivity or specific conductance of an electrolyte solution is the reciprocal of the specific resistivity, ρ, and it can be calculated by measuring the resistance R of the medium between two electrodes of surface A at distance l (figure A1), through equations A4 – A6. [37]

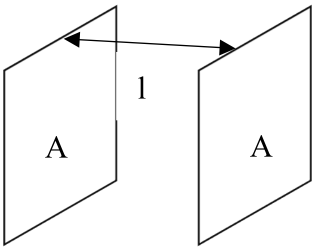

Figure A1.

$$R = \rho\emptyset \text{ (A4)}$$

where:

$\emptyset = \frac{1}{A}$, is the cell constant. The conductivity C is defined by the equation A5 and A6.

$$C = \frac{1}{\rho} \text{ (A5)}$$

$$C = \frac{\emptyset}{\mathbf{R}} \text{ (A6)}$$

Equation A7 deducts the molar conductivity.

$$\Lambda_{\mathrm{m}} = \frac{C}{c} \text{ (A7)}$$

where c is the molar concentration of the electrolytes dissolved in the solution.

For a strong electrolyte, $\mathrm{Y_mZ_n}$, in water, there are anion $\mathrm{Y^{n-}}$ and cation $\mathrm{Z^{m+}}$ completely dissociated, following equation A7.

$$\mathrm{Y_mZ_n} \rightarrow mY^{n+} + nZ^{m-} \text{ (A8)}$$

Kohlrausch's law states that in infinite diluted solutions, the molar ionic conductivity equals the sum of the molar ionic conductivity of the anions and cations present in the solution. The effect of all ions' concentration on conductivity and infinite dilution can be deducted by equation A9 according to Kohlrausch's law. [37]

$$\Lambda^0_{\mathrm{m\,Y_mZ_n}} = \mathrm{n}\lambda_{0\mathrm{Y}} + \mathrm{m}\lambda_{0\mathrm{Z}} \text{ (A9)}$$

where $\lambda_{0\mathrm{Y}}$ and $\lambda_{0\mathrm{Z}}$ are the limiting molar conductivities of the cation Y and anion Z.

The conductivity, C, can be calculated by the equations (A10) introduced by Kohlrausch (Kohlrausch Law), where $\Lambda_{\mathrm{m}(y_mz_n)}$ can be derived by the DHO equation (A11).

$$C_{(y_mz_n)} = \Lambda_{\mathrm{m}(y_mz_n)}\,[Y_m\,Z_n] \text{ (A10)}$$

$$\Lambda_{\mathrm{m}(Y_mZ_n)} = \Lambda^0_{\mathrm{m}(Y_mZ_n)} - \left(\mathbf{A} + \mathbf{B}\Lambda^0_{\mathrm{m}(Y_mZ_n)}\right)c^{0.5} \text{ (A11)}$$

where $\Lambda_{\mathrm{m(Y_m\,Z_n)}}$ is the molar conductivity of the species $\mathrm{Y_mZ_n}$, $\Lambda^{\circ}_{\mathrm{m(Y_m\,Z_n)}}$ is its limiting molar conductivity, **A** and **B** experimental coefficients, $[\mathrm{Y_mZ_n}]$ the molar concentration.

HCl is a strong electrolyte, and the dissociation is complete (A12):

$$HCl \rightarrow H^+ + Cl^- \text{ (A12)}$$

With n = 1, m =1, $\lambda^0_{(\mathrm{H+})}$ = 349,82 S cm^2/mol, $\lambda^0_{(\mathrm{Cl-})}$ = 76.31 S cm^2/mol, $\Lambda^0_{\mathrm{m\ (HCl)}}$ = 425,95 S cm^2/mol, at 25°C and C can be derived from A13. [38]

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$$C_{(HCl)} = \Lambda_{\mathrm{m}(HCl)}\,[HCl] \quad \text{(A13)}$$

where $\Lambda_{\mathrm{m\ (HCl)}}$ is derived by equation A14:

$$\Lambda_{\mathrm{m(HCl)}} = \Lambda^{0}_{\mathrm{m(HCl)}} - \left(\mathbf{A} + \mathbf{B}\Lambda^{0}_{\mathrm{m(HCl)}}\right)c^{0.5} \quad \text{(A14)}$$

where A= 60.20 $\mathrm{cm^2\ dm^{3/2}/\ mol^{3/2}}$ and B = 0.229 $\mathrm{dm^{3/2}/mol^{1/2}}$ at 25 °C. [37]

The impact of the concentration of electrolyte on $\Lambda_{0\ \mathrm{(HCl)}}$ and, therefore, the deviation from the DHO equation is less than 5.0 % for pH less than 1.74 (when [HCl] < 0.018 mol/L). Therefore, the solutions in this paper are in the range of HCl concentrations where the DHO equation is valid.

Following equation A13, we can calculate the theoretical conductivity $C_{\mathrm{(HCl)}}$, according to DHO theory which corresponds to a specific [HCl], and therefore, at the specific pH. (Appendix C) The correlation between $C_{\mathrm{(HCl)}}$ and pH was derived by calculating the pH value corresponding to the specific [HCl] and plotting C as a function of pH. Using XLSTAT statistical software, the best **a** and **b** coefficient of the equation A15 were found:

$$C_{(HCl)} = \boldsymbol{a}\; e^{(-\boldsymbol{b}\, pH)} \quad \text{(A15)}$$

and **a** = 37262.15 and **b** = 2.2555 where determined.

Through equation A15, we can calculate the theoretical conductivity corresponding to one specific pH according to the DHO equation. The deviation of the theoretical model (its accuracy) can be calculated through the percent error between the sample's measured observation and the theoretical value according to the DHO equation. The precision is calculated through the coefficient of variation.

Table A1 reports the coefficients a and b found for the samples, the standard solutions oF HCl, and the DHO model.

Table A1. Comparison between coefficients a and b from regression of samples, standard solution of HCl and DHO model.

	a	**b**
Samples	39117.15	2.2772
Standard solutions HCl	40476.18	2.2897
DHO model	37262.15	2.2555

Appendix-C. Conductivity and pH relationship according to the DHO equation

pH	[H+]	[Cl-]	C C[micro S/mm]
1,56	0,02754229	0,02754229	1101,64
1,57	0,02691535	0,02691535	1077,37
1,58	0,02630268	0,02630268	1053,63
1,59	0,02570396	0,02570396	1030,40
1,60	0,02511886	0,02511886	1007,67
1,61	0,02454709	0,02454709	985,44
1,62	0,02398833	0,02398833	963,68
1,63	0,02344229	0,02344229	942,40
1,64	0,02290868	0,02290868	921,59
1,65	0,02238721	0,02238721	901,22
1,66	0,02187762	0,02187762	881,30
1,67	0,02137962	0,02137962	861,81
1,68	0,02089296	0,02089296	842,74
1,69	0,02041738	0,02041738	824,09
1,70	0,01995262	0,01995262	805,85
1,71	0,01949845	0,01949845	788,00
1,72	0,01905461	0,01905461	770,55
1,73	0,01862087	0,01862087	753,47
1,74	0,01819701	0,01819701	736,77
1,75	0,01778279	0,01778279	720,43
1,76	0,01737801	0,01737801	704,45
1,77	0,01698244	0,01698244	688,82
1,78	0,01659587	0,01659587	673,53
1,79	0,01621810	0,01621810	658,58
1,80	0,01584893	0,01584893	643,95
1,81	0,01548817	0,01548817	629,64
1,82	0,01513561	0,01513561	615,65
1,83	0,01479108	0,01479108	601,97
1,84	0,01445440	0,01445440	588,58
1,85	0,01412538	0,01412538	575,49
1,86	0,01380384	0,01380384	562,69
1,87	0,01348963	0,01348963	550,17
1,88	0,01318257	0,01318257	537,92
1,89	0,01288250	0,01288250	525,94
1,90	0,01258925	0,01258925	514,23
1,91	0,01230269	0,01230269	502,77
1,92	0,01202264	0,01202264	491,57
1,93	0,01174898	0,01174898	480,61

pH	[H+]	[Cl-]	C C[micro S/mm]
2,60	0,00251189	0,00251189	105,06
2,61	0,00245471	0,00245471	102,69
2,62	0,00239883	0,00239883	100,38
2,63	0,00234423	0,00234423	98,11
2,64	0,00229087	0,00229087	95,90
2,65	0,00223872	0,00223872	93,74
2,66	0,00218776	0,00218776	91,62
2,67	0,00213796	0,00213796	89,55
2,68	0,00208930	0,00208930	87,53
2,69	0,00204174	0,00204174	85,56
2,70	0,00199526	0,00199526	83,63
2,71	0,00194984	0,00194984	81,74
2,72	0,00190546	0,00190546	79,89
2,73	0,00186209	0,00186209	78,09
2,74	0,00181970	0,00181970	76,33
2,75	0,00177828	0,00177828	74,60
2,76	0,00173780	0,00173780	72,92
2,77	0,00169824	0,00169824	71,27
2,78	0,00165959	0,00165959	69,66
2,79	0,00162181	0,00162181	68,09
2,80	0,00158489	0,00158489	66,55
2,81	0,00154882	0,00154882	65,04
2,82	0,00151356	0,00151356	63,57
2,83	0,00147911	0,00147911	62,14
2,84	0,00144544	0,00144544	60,73
2,85	0,00141254	0,00141254	59,36
2,86	0,00138038	0,00138038	58,02
2,87	0,00134896	0,00134896	56,71
2,88	0,00131826	0,00131826	55,42
2,89	0,00128825	0,00128825	54,17
2,90	0,00125893	0,00125893	52,95
2,91	0,00123027	0,00123027	51,75
2,92	0,00120226	0,00120226	50,58
2,93	0,00117490	0,00117490	49,44
2,94	0,00114815	0,00114815	48,32
2,95	0,00112202	0,00112202	47,22
2,96	0,00109648	0,00109648	46,16
2,97	0,00107152	0,00107152	45,11

pH	[H+]	[Cl-]	C C[micro S/mm]
3,64	0,00022909	0,00022909	9,71
3,65	0,00022387	0,00022387	9,49
3,66	0,00021878	0,00021878	9,27
3,67	0,00021380	0,00021380	9,06
3,68	0,00020893	0,00020893	8,86
3,69	0,00020417	0,00020417	8,66
3,70	0,00019953	0,00019953	8,46
3,71	0,00019498	0,00019498	8,27
3,72	0,00019055	0,00019055	8,08
3,73	0,00018621	0,00018621	7,90
3,74	0,00018197	0,00018197	7,72
3,75	0,00017783	0,00017783	7,54
3,76	0,00017378	0,00017378	7,37
3,77	0,00016982	0,00016982	7,20
3,78	0,00016596	0,00016596	7,04
3,79	0,00016218	0,00016218	6,88
3,80	0,00015849	0,00015849	6,72
3,81	0,00015488	0,00015488	6,57
3,82	0,00015136	0,00015136	6,42
3,83	0,00014791	0,00014791	6,28
3,84	0,00014454	0,00014454	6,13
3,85	0,00014125	0,00014125	5,99
3,86	0,00013804	0,00013804	5,86
3,87	0,00013490	0,00013490	5,72
3,88	0,00013183	0,00013183	5,59
3,89	0,00012882	0,00012882	5,47
3,90	0,00012589	0,00012589	5,34
3,91	0,00012303	0,00012303	5,22
3,92	0,00012023	0,00012023	5,10
3,93	0,00011749	0,00011749	4,99
3,94	0,00011482	0,00011482	4,87
3,95	0,00011220	0,00011220	4,76
3,96	0,00010965	0,00010965	4,65
3,97	0,00010715	0,00010715	4,55
3,98	0,00010471	0,00010471	4,45
3,99	0,00010233	0,00010233	4,34
4,00	0,00010000	0,00010000	4,25
4,01	0,00009772	0,00009772	4,15

pH	[H+]	[Cl-]	C C[micro S/mm]
4,68	0,00002089	0,00002089	0,89
4,69	0,00002042	0,00002042	0,87
4,70	0,00001995	0,00001995	0,85
4,71	0,00001950	0,00001950	0,83
4,72	0,00001905	0,00001905	0,81
4,73	0,00001862	0,00001862	0,79
4,74	0,00001820	0,00001820	0,77
4,75	0,00001778	0,00001778	0,76
4,76	0,00001738	0,00001738	0,74
4,77	0,00001698	0,00001698	0,72
4,78	0,00001660	0,00001660	0,71
4,79	0,00001622	0,00001622	0,69
4,80	0,00001585	0,00001585	0,67
4,81	0,00001549	0,00001549	0,66
4,82	0,00001514	0,00001514	0,64
4,83	0,00001479	0,00001479	0,63
4,84	0,00001445	0,00001445	0,62
4,85	0,00001413	0,00001413	0,60
4,86	0,00001380	0,00001380	0,59
4,87	0,00001349	0,00001349	0,57
4,88	0,00001318	0,00001318	0,56
4,89	0,00001288	0,00001288	0,55
4,90	0,00001259	0,00001259	0,54
4,91	0,00001230	0,00001230	0,52
4,92	0,00001202	0,00001202	0,51
4,93	0,00001175	0,00001175	0,50
4,94	0,00001148	0,00001148	0,49
4,95	0,00001122	0,00001122	0,48
4,96	0,00001096	0,00001096	0,47
4,97	0,00001072	0,00001072	0,46
4,98	0,00001047	0,00001047	0,45
4,99	0,00001023	0,00001023	0,44
5,00	0,00001000	0,00001000	0,43
5,01	0,00000977	0,00000977	0,42
5,02	0,00000955	0,00000955	0,41
5,03	0,00000933	0,00000933	0,40
5,04	0,00000912	0,00000912	0,39
5,05	0,00000891	0,00000891	0,38

pH	[H+]	[Cl-]	C [micro S/mm]
5,75	0,00000178	0,00000178	0,08
5,76	0,00000174	0,00000174	0,07
5,77	0,00000170	0,00000170	0,07
5,78	0,00000166	0,00000166	0,07
5,79	0,00000162	0,00000162	0,07
5,80	0,00000158	0,00000158	0,07
5,81	0,00000155	0,00000155	0,07
5,82	0,00000151	0,00000151	0,06
5,83	0,00000148	0,00000148	0,06
5,84	0,00000145	0,00000145	0,06
5,85	0,00000141	0,00000141	0,06
5,86	0,00000138	0,00000138	0,06
5,87	0,00000135	0,00000135	0,06
5,88	0,00000132	0,00000132	0,06
5,89	0,00000129	0,00000129	0,05
5,90	0,00000126	0,00000126	0,05
5,91	0,00000123	0,00000123	0,05
5,92	0,00000120	0,00000120	0,05
5,93	0,00000117	0,00000117	0,05
5,94	0,00000115	0,00000115	0,05
5,95	0,00000112	0,00000112	0,05
5,96	0,00000110	0,00000110	0,05
5,97	0,00000107	0,00000107	0,05
5,98	0,00000105	0,00000105	0,04
5,99	0,00000102	0,00000102	0,04
6,00	0,00000100	0,00000100	0,04
6,01	0,00000098	0,00000098	0,04
6,02	0,00000095	0,00000095	0,04
6,03	0,00000093	0,00000093	0,04
6,04	0,00000091	0,00000091	0,04
6,05	0,00000089	0,00000089	0,04
6,06	0,00000087	0,00000087	0,04
6,07	0,00000085	0,00000085	0,04
6,08	0,00000083	0,00000083	0,04
6,09	0,00000081	0,00000081	0,03
6,10	0,00000079	0,00000079	0,03
6,11	0,00000078	0,00000078	0,03
6,12	0,00000076	0,00000076	0,03
6,13	0,00000074	0,00000074	0,03

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