

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

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1) Materials

Table S1 shows the commercial additives in Tables 4 and 5 of the paper, S2 the test apparatuses, and S3 the test methods.

Table S1: Raw Materials

Raw Materials
Inovyn 271 PC: PVC S K70 produced by Inovyn. https://www.ineos.com/businesses/inovyn/
Diplast N: Di Iso Nonyl Phthalate produced by Polynt S.p.A.. https://www.polynt.com/it/
Reaflex EP/6: Epoxidized Soy Bean Oil (ESBO) in the product portfolio of Reagens. https://www.reagens-group.com/
Arenox A10: Pentaerythritol tetrakis(3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate) in the product portfolio of Reagens. https://www.reagens-group.com/
RI004: Antimony trioxide from Quimialmel: https://quimialmel.it/
Riochim: Ground Calcium Carbonate produced by Umbriafiller: https://umbriafiller.com/
Omya 95 T: Ground Calcium Carbonate produced by Omya: https://www.omya.com/en/industries/polymers
Winnofil S: Precipitated Calcium Carbonate in the product portfolio of Imerys: https://www.imerys.com/
AS-1B, AS-6B: Acid scavengers at high temperatures acting in the condensed phase from Reagens S.p.A. https://www.reagens-group.com/
Apyral 40 CD: Synthetic aluminum tri hydroxide, produced by Nabaltec. https://nabaltec.de/en/
Ecopypren 3.5: Brucite in the product portfolio of Europiren. https://europiren.com/it/catalog/ecopipren/
Reapak B-CV/3037: Thermal stabilizer in the product portfolio of Reagens. https://www.reagens-group.com/

Table S2: Apparatuses

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	

Table S3. Technical Standards.

Technical standard	Measurement	Temperature [°C]	Note
Internal method 4	Multimeter	Isothermal at 950 °C	DDW, pH, and Conductivity.
	pH and Conductivity		The general method, according to the 2014 version.
	IC	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⁻
	Anions and cations		
	ICP-OES	Isothermal at 950 °C	Mg, Al, Ca, Zn, Sb
	Elements		
Internal method 5	Multimeter	Thermal profile of EN 60754-1 ¹	DDW, pH, and Conductivity.
	pH and Conductivity		The general method, according to the 2014 version.
	IC	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⁻
	Anions and cations		
	ICP-OES	Thermal profile of EN 60754-1 ¹	Mg, Al, Ca, Zn, Sb
	Elements		

2) Sample preparation

In summary, the formulations in Tables 4 and 5 of the paper are mixed in a turbo mixer with plasticizer added at 80°C, up to 105 °C. Dry blends were cooled, then processed into kneaders (60 g in plasticorder for 10 minutes at 160°C, 30g/m). The kneaders are pressed in 0.5 mm plaques in a hydraulic press, (160°C per 1.5 min, 20 bar, 160°C per 1.5 min at 60 bars, 160°C per 1 min at 100 bars, cooling cycle at 150 bar). Then plaques 0.5 mm thick were obtained and test specimens processed applying internal method 4 and 5.

3) Measurements of the main properties

The data have been reported in Tables 8, 13 and 22 of the article.

3.1) Internal Method 4 procedures

The tube furnace (SA Associates, Table S2) has a touch screen temperature controller through which the heating regime of EN 60754-2 [1] was selected (isothermal at 950 °C). The final temperature was checked and adjusted with a calibrated external thermocouple. According to the quartz tube dimensions, the airflow was set at 300 ml/min +/- 10 ml/min, as EN 60754-2 requested. Before the first run, a preliminary bubbling test in the devices was done to verify that all connections were well-tightened and that no HCl leak could affect the measurements. The kneaders were conditioned for 24 h at 23°C. Slices with similar dimensions for all runs (approximately 1 mm x 1 mm) were derived from them. The slices were weighed into the combustion boat and arranged in the tube furnace when the temperature was stable at 950 +/- 5 °C.

Smokes were collected in two bubbling devices containing double deionized water produced by Ion Exchange Deionizer (Table S2) of the quality required by EN 60754-2 for 30 minutes. The two quotes were collected in a 1 L volumetric flask, ensuring all connectors and bubbling devices were well-cleaned to recover as much HCl as possible.

Three filtered quotes for each sample were taken from the volumetric flash. The first for pH and conductivity measurements, the second for IC, the third for ICP-OES.

pH and conductivity were measured simultaneously by inserting the electrodes in two different vessels. pH and conductivity measures are taken at 25 °C +/- 1 with the following procedure: the multimeter has been calibrated with standard solutions before each measurement: pH at two points (4.01 and 7.00) and conductivity at 1 point at 141.3 µS/mm. The solutions closest to the measured value have been chosen as correction standards, and the measurements are corrected accordingly through a correction factor. pH and conductivity electrodes have a reference thermocouple that adjusts the temperature fluctuation. pH and conductivity are measured, and two replicates give the mean value, standard deviation (SD), and coefficient of variation (CV).

Ion chromatography (IC) was conducted, and the mean of two measurements was determined, ensuring a minimal difference of less than 0.1 mg/g and a ratio between the mean and standard deviation of less than 0.25. The procedures adhered to ISO 10304-1 for anion detection [2] and ISO 14911 for cations. [3] Without the need for sample pre-treatment, the standard specified the following lower application limits:

For Anions:

- Bromine and nitrite: ≥ 0.05 mg/L
- Chlorine, fluorine, nitrate, orthophosphate, and sulfate: ≥ 0.1 mg/L

For Cations:

- Lithium: ≥ 0.01 mg/L
- Sodium, ammonium, and potassium: ≥ 0.1 mg/L
- Magnesium and calcium: ≥ 0.5 mg/L

ISO 10304-1 and ISO 14911 are designed to detect analytes below 10 mg/g. Modifications were made to some procedures to accommodate dosing anions and cations at concentrations up to 200 mg/g.

Inductively coupled plasma optical emission spectroscopy (ICP-OES) was performed following protocol 11885 [4] for the detection of Al, Zn, and Sb. The limits of quantification (LOQ) at the specific used wavelengths are as follows:

- Antimony and calcium: ≥ 0.1 mg/L
- Zinc and magnesium: ≥ 0.0033 mg/L
- Aluminum: ≥ 0.001 mg/L.

3.2) Internal Method 5

The tube furnace (SA Associates, Table S2) has a touch screen temperature controller through which the heating regime of EN 60754-1 [5] has been selected (Table S3). The check of the temperature regime has been done following this procedure. An empty combustion boat is introduced in the tube furnace through the sample carrier. The airflow is set between 290 and 310 ml/min according to the quartz tube geometry. The thermocouple is inserted in the center of the tube furnace, the initial ramp is chosen, the heater is started, and the time is followed with a stopwatch. The ramp is chosen for reaching 800 °C +/- 10 °C in 40 min +/- 5 min and for keeping an isothermal condition of 800 °C +/- 10 °C per 20 min +/- 1 min. The heating rate is adjusted

accordingly if temperatures and times exceed the above ranges. The conductivity of the water in the bubblers is checked to verify the possibility of contamination from previous tests.

After determining the heating regime and the cleaning status of the quartz tube, the sample is weighed in the combustion boat (1.000 g \pm 0.001 g of material) and introduced in the tube furnace at room temperature through the sample carrier. The heater is switched on, and the stopwatch checks the ramp. After 1 hour, the connectors are opened, and the water from the bubbling devices and washing procedures is collected in a 1 L volumetric flask filled to the mark. pH and conductivity are measured (as described in paragraph 3.3.1), and two replicates give mean value, standard deviation (SD), and coefficient of variation (CV).

Ion chromatography (IC) was conducted, and the mean of two measurements was determined, ensuring a minimal difference of less than 0.1 mg/g and a ratio between the mean and standard deviation of less than 0.25. The procedures adhered to ISO 10304-1 for anion detection and ISO 14911 for cations. Without the need for sample pre-treatment, the standard specified the following lower application limits:

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- Magnesium and calcium: ≥ 0.5 mg/L

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- Zinc and magnesium: ≥ 0.0033 mg/L
- Aluminum: ≥ 0.001 mg/L.

References

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