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Toward Silica-Free Compliance: A Low-Viscosity Sample Pretreatment Methodology for Crystalline Quartz Quantification in Viscous Pastes

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ABSTRACT

Crystalline quartz, the most common crystalline silica polymorph, is widely found in industrial products. It is of high regulatory relevance, because its fine fraction, a form of respirable crystalline silica, is classified as an occupational carcinogen, with product-content thresholds (e.g., 0.1% (w/w) in the European Union) and stringent occupational exposure limits. Since larger size fractions can be reduced to the fine one during work processes and use, a silica-free approach should be pursued, driving the need for accurate and sensitive quantification of crystalline quartz, even in complex matrices. X-ray diffraction (XRD) is a reference technique for selective quartz determination; however, paraffin-rich abrasive and polishing pastes pose a major analytical challenge due to their dense, viscous rheology, which prevents homogeneous incorporation of crystalline internal standards or spikes required by validated quantitative XRD approaches (e.g., EN 13925, EN 17289). Here, we develop and optimize a low-viscosity sample pretreatment, termed low-viscosity doping (LVD), to overcome matrix-driven inhomogeneity. LVD mitigates rheological constraints, enables uniform internal-standard distribution, and improves the reliability of quantitative XRD. Using LVD, crystalline quartz mass fractions were determined with good accuracy and repeatability at levels well below the 0.1% product threshold. The proposed workflow is standardized, time-efficient, and compatible with modern benchtop diffractometers, potentially paving the way for a standard aimed at enhancing safety compliance and risk mitigation in the abrasive and polishing products industry.

1 | Introduction

Respirable crystalline silica (RCS), particularly its polymorphs quartz, cristobalite, and tridymite, is recognized as an established occupational carcinogen (IARC Group 1) and a significant driver of fibrotic lung disease. Inhalation of RCS is associated with the development of numerous conditions, the most severe one being silicosis [1–4], an irreversible lung disease ultimately leading to mortality (Figure SM-1a in S1) [5, 6]. Crucially, aside from lung transplantation, effective treatments for silicosis remain unavailable. This dire outcome could be prevented by

reducing or eliminating occupational exposure to RCS and improving our environment [7].

For these reasons, regulatory bodies worldwide have imposed stringent permissible exposure limits (PELs) on the levels of RCS fraction in occupational workplaces with values lower than 0.1 mg/m³, e.g., 2004/37/EC [8, 9]. Despite these health hazards, RCS is an intrinsically pervasive and essential component of modern industrial economies, with its presence woven throughout numerous manufacturing and industrial sectors, including construction, mining, ceramics, and material finishing (Figure

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SM-1b in S1) [4]. Although the global impact of occupational silica exposure is only partially documented in these sectors, the persistently elevated levels reported underscore the magnitude of the public health crisis [10–12], urging the use of alternative materials, wherever technically feasible [13, 14].

The fundamental challenge in regulatory compliance and risk mitigation lies in monitoring RCS and preventing its formation from CS-containing materials during production/manufacturing processes [15]. CS refers to the crystalline phase in general, while RCS comprises only airborne CS particles with an aerodynamic diameter less than or equal to $10\mu\text{m}$, capable of penetrating deep into the alveoli of the lungs (Figure 1) [3]. Despite the complexity of classification under regulations like REACH (EC No. 1907/2006) for unprocessed natural materials containing quartz, industrial mineral producers in the EU (IMA) proactively classified materials based on their fine CS content, according to the globally harmonized system (GHS) and specific target organ toxicity upon repeated exposure (STOT RE) [16]. Similar actions were taken in the USA and China, although with different thresholds. These efforts show how regulatory frames are focusing on RCS fractions—a minimal though carcinogenic fraction as shown in Figure 1B—while having a limited consideration of its source, the CS [5].

The capability to determine CS at low mass fraction levels is thus instrumental in making the current and future regulations effective. In the last years, the occupational risk assessment, predominantly relying on monitoring RCS concentration in the air [9, 17], has progressively been supported by a proactive *silica-free* approach: the source materials (powders) [18] used in production processes are analyzed to prevent the potential release of hazardous dust, as established by the European Regulation (EC) No. 1272/2008, which sets a mass fraction limit of 0.1%. Similarly, 29 CFR 1910.1200 and GB 15258 set rules in the USA and China, respectively.

Within this regulatory and safety frame, abrasive and polishing pastes represent a highly relevant and analytically challenging product group. These formulations are critical across a multitude of sectors, from high-precision engineering for surface refinement to high-throughput automotive and esthetic finishing [19, 20]. Polishing pastes are complex semisolid mixtures,

typically consisting of a dispersive phase, often paraffin-based, and an abrasive phase of mineral particles [21]. Their classification is based on the chemical identity and particle size of the abrasive, which dictate the final surface finish [22]. Historically, the abrasive phase frequently contained natural emery, a hard, dark granular rock composed predominantly of corundum (Al_2O_3) and iron oxides (magnetite/hematite) [23–25], with a variable crystalline silica (quartz) content, typically at mass fractions of about 4%, which is well above the 1.0% threshold for STOT RE 2 classifications [26]. While manufacturers are increasingly shifting to synthetic, silica-free alternatives to meet *silica-free* policies, the regulatory and commercial need to confirm the effective CS mass fraction in finished pastes remains paramount. Figure 2 descriptively illustrates two distinct but highly integrated methods for assessing the exposure risk stemming from CS, specifically focusing on the most hazardous polymorphs: quartz, cristobalite, and tridymite, which may be present in polishing abrasive pastes.

The first approach, depicted in Figure 2A, focuses on verifying process safety by measuring the actual RCS fraction (particle size $\leq 10\mu\text{m}$) generated during operation. Analysis of the RCS confirms current exposure levels. If this measurement exceeds an adequate limit of detection (LOD), it is a red flag that mandates further investigation, including testing the bulk material, to precisely identify the source contaminating the air. Conversely, the second approach, shown in Figure 2B, involves the proactive environmental screening of the pastes themselves to quantify all three CS polymorphs. This test is designed to identify whether the source material is a potential environmental hazard capable of releasing respirable dust. A positive result (exceeding the LOD) means the paste is deemed high-risk and requires mandatory substitution with safer, *silica-free* alternatives, e.g. [14]. In essence, air monitoring (Figure 2A) confirms safety during use, while source material analysis (Figure 2B) facilitates fundamental material substitution. The complementary use of these two analyses is essential for an effective and health-protective *silica-free* approach. Despite the recognized importance of accurate monitoring across all sectors, the overall analytical landscape for both airborne and bulk crystalline silica remains complex and challenging, highlighting the need for continuous method development and critical evaluation of existing measurement techniques to ensure regulatory compliance

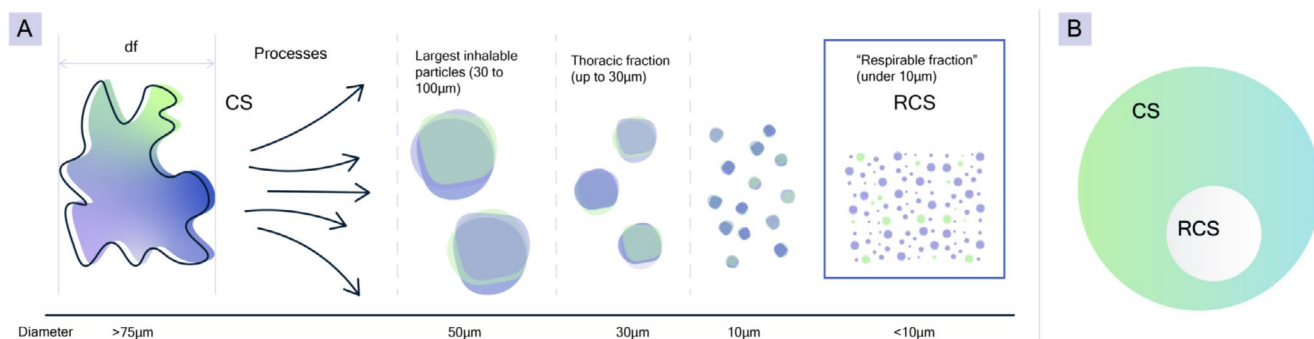


FIGURE 1 | Relation between CS and RCS. (A) the successive, multiple size-selection processes that correlate CS and RCS particle fractions, starting from bulk material containing CS particle with a diameter $>75\mu\text{m}$, toward a progressive size reduction till most hazardous particles under $10\mu\text{m}$. (B) RCS fraction is a critical subset of the larger CS particle content; therefore, the presence of CS can potentially generate RCS while determining RCS fraction does not assure the absence of CS particles. [Colour figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

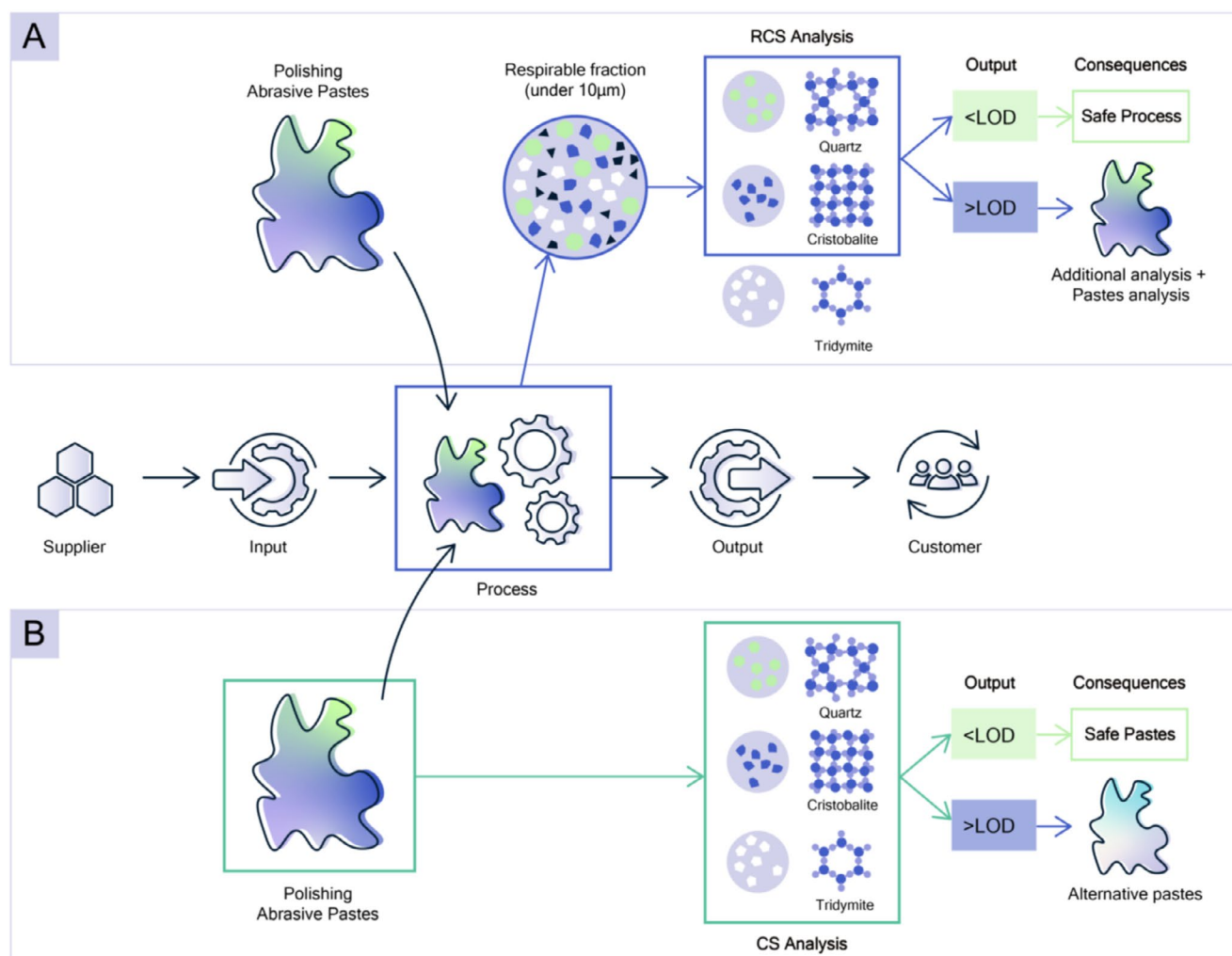


FIGURE 2 | Two analytical strategies for managing potential exposure to RCS stemming from polishing and/or abrasive pastes. (A) RCS analysis (environmental monitoring): focuses on the respirable fraction generated during the process and (B) CS analysis (bulk material testing): directly analyzes the pastes to quantify all three CS polymorphs (quartz, cristobalite, and tridymite). [Colour figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

and worker safety [26]. In this view, accurate quantification of CS polymorphs is essential for robust risk assessment.

X-ray diffraction (XRD) is the gold-standard analytical technique for this purpose, offering high specificity for crystalline phases and forming the basis for dedicated standards like the EN 17289 [27] series for bulk materials, and the ISO 16258 [28] and ISO 24095 [29] standards for airborne dust. Actually, these standards for RCS analysis focus on quartz and cristobalite, because tridymite occurrence is less frequent and also poses analytical difficulties. XRD provides superior precision and accuracy in identifying and quantifying CS phases like α -quartz, even in complex dust samples, and is often preferred over techniques like FTIR or Raman spectroscopy for well-characterized silicates [26]. Its ability to cover a wider sample analysis area also contributes to greater reliability by mitigating uncertainties related to laborious pretreatment steps [30]. Moreover, in addition to traditional XRD analytical methods, like those based on calibration curves for RCS on filters, quantitative Rietveld refinement has progressively been applied for multiphase samples analysis, allowing minimization of some of the issues affecting single-peak calibration approaches, i.e., preferred orientation,

peak overlap, and matrix absorption [31, 32]. Since the detection capabilities are ultimately dependent on the signal-to-noise ratio (SNR), X-ray diffractometers maximize the counting statistics either with high power X-ray sources (floor-standing instruments) or with intensity-tailored optical configurations and linear or 2D detectors (benchtop instruments). These systems utilize low power X-ray generators (300–600 W instead of 3000 W) coupled with traditional X-ray tubes, with the advantage of increasing their lifetime, simplifying their operation (no external cooling or dedicated power supply needed), and providing SNR comparable to larger instruments. This accessibility makes them appealing for environmental laboratories and quality control and routine monitoring in manufacturing environments. Despite the difference in scale and power, both classes of instruments mostly rely on the internal standard (IS) addition methods for accurate quantitative analysis, because it allows taking into account the possible presence of amorphous material and thus provides an unbiased quantification for crystalline phases. Alternatively, dedicated calibration curves, specific to the type of matrix under investigation, are built [33]. Usually, a small-granulometry powder is used as an internal standard or spike. Recently, Mecchia et al. [15] published the outcomes of an inter-laboratory study

demonstrating the equivalence of the external standard, internal standard and spiking methods for the quantification of crystalline quartz, with mass fraction ranging between 10% and 16%, in binary mixtures of powders. However, when it comes to the complexity of the polishing paste matrix, the analytical method faces a challenge: the viscous, dense, semisolid, or liquid consistency of the paste, related to the substantial presence of semicrystalline paraffin and its derivatives, makes the homogeneous dispersion of low-granulometry powder difficult.

This study directly addresses this critical analytical gap by proposing a heating pretreatment methodology—namely, the low-viscosity doping (LVD)—specifically designed to overcome the inherent issues posed by the viscous matrix of abrasive and polishing pastes. To the authors' knowledge, no application of the mentioned heating procedure for this type of samples has been done before to determine the crystalline silica content, in the context of the currently available norms, especially EN 17289 and ISO 24095. Our investigation evaluates the efficacy of this pretreatment in achieving reliable and repeatable quantification of minor levels of quartz, the most frequent CS polymorph, in three distinct commercial polishing pastes, consisting of a paraffin matrix with dispersed corundum abrasive powder. Crucially, we demonstrate the method's robustness by applying it successfully across both a high-power floor-standing diffractometer and an accessible low-power benchtop diffractometer. Initial qualitative analysis was performed to search for the possible presence of CS, followed by incremental spiking of a blank sample with quartz to assess the linearity of the response of the diffraction signal. Finally, quantitative determination using the method of standard additions, as recommended by EN 17289, was performed for two samples showing a little amount of quartz. By establishing a standardized procedure that accommodates modern and accessible benchtop instrumentation, this work enriches the XRD toolbox for *silica-free* design of industrial and crafted productions using polishing and abrasive pastes with paraffin matrix.

2 | Materials and Methods

2.1 | Reagents and Samples

Three polishing paste samples (S1, S2, S3) were obtained from commercial sources (generic description in Table SM-1 in S1). For accurate quantitative analysis of quartz in the pastes, which did not exhibit cristobalite or tridymite peaks, a method of standard additions was employed, consistent with the recommendation of EN 17289. Due to the high cost and limited availability of certified reference materials (specifically NIST SRM 1878b for respirable quartz and SRM 1879b for cristobalite), suitable, more accessible replacements were identified in accordance with ISO 16258-1 and guidance by Stacey et al. [34]. The spiking material was pure quartz P3 ($\text{SiO}_2 = 99.1\%$, median particle size of $3\mu\text{m}$), supplied by Minerali Industriali (Novara). The material used for the initial approximate estimation of quartz content was pure ZnO (zincite, purity greater than or equal to 99.9%, particle size less than $5\mu\text{m}$), purchased from Merck (product number 205532). The crystallinity of both the quartz P3 and ZnO powders was rigorously determined by realizing binary mixtures of each with known amounts of two certified crystallinity

reference materials (NIST SRM 1879b and SRM 676a) to better assess measurement uncertainty [35]. The resulting binary mixtures were homogenized using a Retsch vibratory mill (MM400) equipped with 25 mL zirconium oxide jars, deemed suitable for the hardness of the involved powders. In order to avoid any possible detrimental effect on crystallinity, no grinding balls were added, while the homogenization time and frequency were set at 5 min and 15 Hz, respectively.

2.2 | LVD

The LVD was developed to address the challenging matrix of polishing pastes. It involves heating the paste to reduce its viscosity, allowing for direct doping with either zinc oxide or quartz. This approach aims to maintain the original sample matrix while ensuring a homogeneous dispersion of the additional powder. Approximately 3 g of the polishing paste sample was accurately weighed in a 30 mL borosilicate glass vial with a phenolic screw cap, placed in an analytical balance with 0.1 mg readability. A known amount of ZnO (about 0.2 g) was added to the vial. The mass ratio of ZnO to sample was optimized through preliminary experiments to ensure appropriate peak intensities for accurate quantification, without interfering too much with nearby peaks. The sealed vial was then heated by immersion in a water bath on a hot plate at $60^\circ\text{C} \pm 10^\circ\text{C}$ for a duration sufficient to fully liquefy the paste (typically between 5 and 10 min), facilitating a significant reduction in viscosity. Immediately after heating, the vial was homogenized using a vortex mixer for 20 s to ensure thorough dispersion of ZnO within the paste. Heating and mixing of the spiked sample were repeated for each single sample deposition for XRD analysis, to ensure the matrix had approximately the same reduced viscosity and the variability at the preparation stage was comprised in the following acquisitions. Although the median particle size of ZnO was appropriate to minimize gravitational segregation within the liquid paste, single aliquots for deposition were taken with a Pasteur pipette immediately after mixing, i.e., within 10 s. The deposition was done in a front-loading sample holder with a cavity of 0.8 mm and a diameter of 22 mm. In this case, the paste was gently pressed and spread within the cavity using a frosted glass slide, ensuring the surface was flush with the reference plane of the sample holder. The samples for the standard additions were prepared weighing approximately 10 g of the polishing paste in a 30 mL borosilicate glass vial with a phenolic screw cap and adding three different quantities of the highly pure quartz, equal to 0.5, 1, and 2 times the initial estimation of quartz respectively (EN 17289-1). As done after the ZnO addition, the samples were heated, homogenized using a vortex mixer and deposited in the sample holder cavity. Considering the fusion temperature of paraffin ($\sim 40^\circ\text{C}$), the limited sample mass and the apparent change in physical behavior when melted, the procedure was simple and robust enough to allow three different operators to perform it, even with different hot plates, balances, vortex mixers and pipetting skills.

2.3 | Instrumentation

XRD patterns were acquired using both high and low-power X-ray diffractometers, Explorer (GNR s.r.l., Novara, Italy) and

D2 Phaser (Bruker AXS, Karlsruhe, Germany), respectively. Both diffractometers were equipped with a Fine Focus Cu X-ray source, whose characteristic radiation is made of two main emission lines, $\lambda(K\alpha_1) = 1.5406 \text{ \AA}$ and $\lambda(K\alpha_2) = 1.5444 \text{ \AA}$, and smaller third emission line $\lambda(K\beta_1) = 1.3922 \text{ \AA}$. The latter was suppressed by either a 0.02 mm Ni filter (Explorer) or by the detector energy threshold (D2). Explorer, characterized by a 240 mm-radius goniometer and an Advacam Minipix 2D detector in 1D mode, was operated at the standard power settings of 1200 W (40 kV and 30 mA). D2, mounting a LYNXEYE XE-T 2D detector in 1D mode, was operated at 300 W (30 kV and 10 mA), which makes it one of the lowest power diffractometers on the market. In both instruments, the sample was hosted in a front-loading sample holder on a rotating sample stage. For a first assessment of the crystalline phases present in the paste, data were collected from 15° to 75° (2θ) at $1^\circ/\text{min}$ with Explorer and $2.4^\circ/\text{min}$ with D2. Table 1 summarizes the instrumental setup details, while Figure 3 shows a schematic of the setup parameters for the two different X-ray diffractometers employed in this work. All the measurements were performed at room temperature (25°C).

A first quantitative analysis of quartz in samples was performed using the internal standard method by adding a known amount of zincite (ZnO). Both Rietveld refinement and simple reference intensity ratio (RIR) quantification were carried out. For RIR and standard additions, the acquisition of diffractograms was limited to regions of interests (ROI) centered on the primary peaks of quartz (101) at $2\theta = 26.63^\circ$ and zincite (101) at $2\theta = 36.25^\circ$, to have a good trade-off between the measurement time and the detection capabilities. ROIs of 2° were collected in static mode for 600 s with Explorer, while in scanning mode for 1900 s with D2.

First phase identification and RIR quantification were performed by Match! (Crystal Impact, Bonn), DIFFRACT.EVA (Bruker AXS, Karlsruhe), and ICDD PDF-5+ database. Peak area determination and Rietveld refinement were performed by the freely available Profex software [36], taking into account both $K\alpha_1$ and $K\alpha_2$ contributions. As a matter of fact, since the software is provided with a full-profile search and match

algorithm and the possibility of accessing the free crystallography open database [37], it may be used even for checking the crystalline phases, thus making the proposed protocol suitable to users with limited economic resources.

3 | Results and Discussion

3.1 | Determination of Quartz and Zincite Crystallinity: The Internal Standard Method

To use the zinc oxide and quartz powders as internal standard and spikes, respectively, their actual amount in the chosen products had to be determined. In fact, the possible presence of amorphous material or other minor crystalline phases cannot be excluded, which would inevitably bias the following estimations based solely on experimental intensity ratios. Thus, both quartz and zinc oxide powders were mixed with a known amount of a certified reference material (w_{IS}) to estimate their crystalline phase percentage (crystallinity), according to the internal standard method. The procedure requires that first the mass fractions of the crystalline phases (w'_j) and internal standard (w'_{IS}) are determined in the new sample (original plus internal

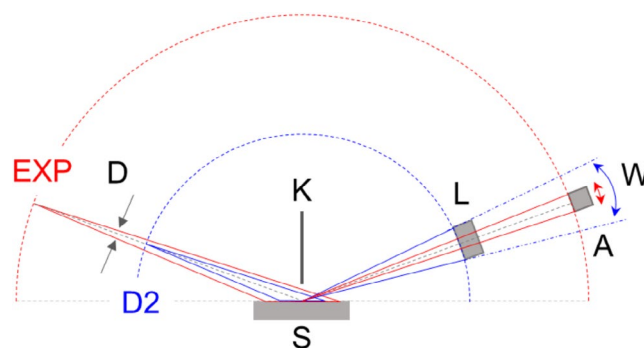


FIGURE 3 | Schematic of the different setup parameters of D2 (blue circle) and Explorer (red circle). A, Advacam detector; D, divergence; K, anti-scatter shield; L, LynxEye detector; S, sample; W, detector active region. [Colour figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/xrs.70128)]

TABLE 1 | Instrumental setup for Explorer and D2 diffractometers.

	Explorer (high power)	D2 (low power)
Goniometer radius (mm)	240	141
Divergence slit (mm)	0.8	1
Incident beam soller slit ($^\circ$)	2.3	2.5
Antiscatter shield	Yes	
Sample rotation (rpm)	30	15
Diffracted beam soller slit ($^\circ$)	2.3	4
Detector active region ($^\circ$)	2	5.8
Detector sensor area (mm^2)	14×14	14.4×16
Detector equatorial pixel pitch (μm)	55	75
Cu $K\beta$ suppression	Ni filter (0.02 mm)	Detector energy threshold
Optimized for	Angular resolution	Signal intensity

standard), assuming it is completely crystalline: these can be determined either by RIR or Rietveld refinement analysis [33], by relying on experimental diffraction peaks and scattering factors. Finally, the ratio (w'_{IS}/w_{IS}) is used to provide an estimation of the actual crystalline mass fraction of the phase of interest in the original sample. It must be pointed out that the internal standard method is not affected by matrix effects because it is based on ratios of intensities, where the mass attenuation coefficient is flushed out (Section S2 in S1).

Following the outlined procedure, the cristobalite (NIST SRM 1879b) internal standard amount w_{IS} was about 4%–5% for both products, while the corundum (NIST SRM 676a) one was 18% for quartz and 27% for zincite. The mean values of crystallinity, calculated with Rietveld refinement of the mixtures of the products with each SRM, were $(87 \pm 3)\%$ and $(90 \pm 1)\%$ for quartz and zincite, respectively (Section 3 in S1). The reported uncertainty for crystallinity, 1σ standard deviation, was considered in the following calculations. The initial structural parameters were taken from ICDD PDF5+ 040042852 (corundum), 010710785 (cristobalite), 040150825 (zincite) and 040087651 (quartz).

3.2 | Characterization of the Polishing Pastes

Polishing pastes are complex formulations comprising solid abrasive particles, organic binders, solvents, and various additives, often forming a nonuniform suspension. The inherent

heterogeneity of these matrices makes their characterization—especially for quantitative analysis—challenging. XRD analysis of the pastes revealed a variegated mineralogical composition reflecting the multicomponent nature of these materials characterized by abrasive and dispersing phases. The initial characterization was performed with Explorer, to have the maximum available flexibility as regards angular resolution and power. Figure 4a shows a representative diffraction pattern of a polishing paste (sample S1) with a predominant crystalline phase of corundum—the abrasive component—and the presence of semicrystalline paraffin—the dispersing phase. Neither quartz nor cristobalite peaks were detected. The X-ray transparency of the light matrix and the small sample displacement error (SDE) [38], due to the contraction of the paste height in the cavity after cooling, were not an issue for the identification of the phases and could be dealt with easily by the software. The predominant phase, corundum ($\alpha\text{-Al}_2\text{O}_3$), is characterized by the main reflections at approximately $2\theta = 35.15^\circ$ (104) and $2\theta = 43.3^\circ$ (113) (ICDD PDF 04-005-4505). Reflections attributable to crystalline paraffin were observed around $2\theta = 21.48^\circ$ (corresponding to the (110) plane of orthorhombic paraffin) and $2\theta = 23.85^\circ$ (ICDD PDF 00-040-1995). It is worth noting that the exact position and intensity of the reflections depend on the paraffin's purity and degree of ramification [39].

The high viscosity of these samples makes it difficult to obtain a truly representative aliquot for XRD analysis; mixing prior to analysis might not fully homogenize the sample, and even

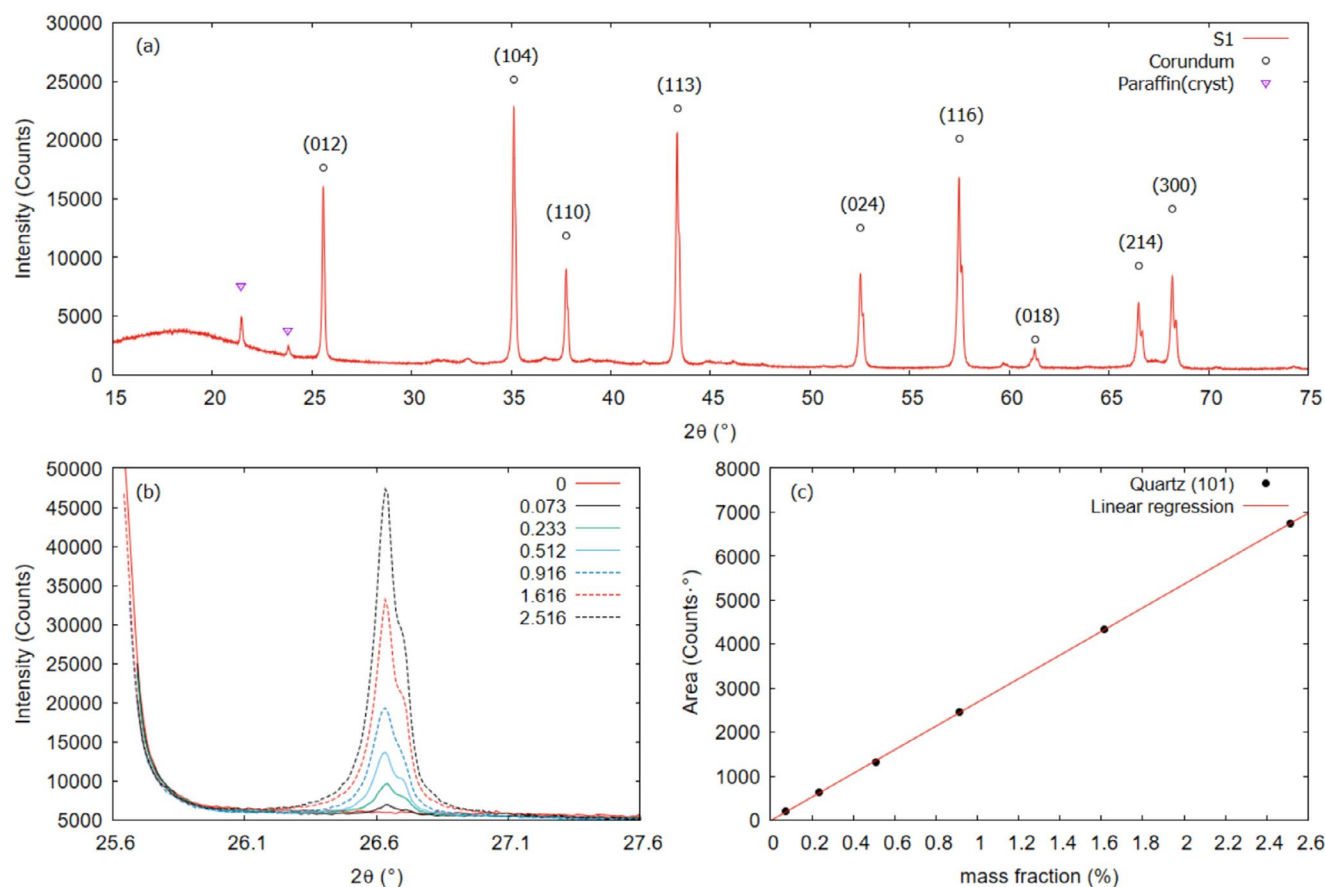


FIGURE 4 | Diffraction pattern for sample S1 (a); progressive addition of quartz to S1 and related (101) peak increase (b); linear regression for quartz (101) peak area versus the quartz mass fraction (c). [Colour figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

small variations in sample preparation might lead to significant discrepancies in results. Additionally, the predominantly amorphous matrix is responsible for a high background in the diffractogram, further complicating the detection and quantification of minor crystalline phases. These characteristics complicate the application of standard quantitative XRD methods, such as the internal standard method or the standard addition method required by EN 17289-1. Both approaches rely on the assumption that the added standard (or analyte in standard addition) is uniformly distributed within the sample matrix and behaves identically to the existing components. However, with highly viscous samples like pastes, this assumption is generally not applicable due to their inherent nonhomogeneity, necessitating a specific sample preparation procedure to ensure accurate results. To address this, the LVD method described in Section 2.2 was developed.

The applicability of this pretreatment procedure was first tested operating multiple addition of quartz ($87\% \pm 3\%$ crystallinity) to sample S1, with the aim of evaluating the linearity of the (101) peak area at increasing analyte mass fraction. If the added amount is limited, i.e., up to a few percent, the variation of the mass attenuation coefficient is negligible and thus the expected signal is a linear function of the mass fraction (Equation 1 in S1), provided the phase is homogeneously distributed in the sample. The results, obtained with Explorer and reported in Figure 4b, show the region of the primary reflection of quartz ($2\theta = 26.63^\circ$) after the addition of six increasing aliquots in the range between 0.073% and 2.516% (w/w). The least squares method applied to the peak area versus the mass fraction provided a line (Figure 4c) with a coefficient of determination R^2 equal to 0.9999, slope equal to (2688 ± 13) Counts $^\circ$ /%, and intercept equal to (-11 ± 16) counts $^\circ$, which is not significantly different from a zero-intercept line; moreover, the applicability of the linear model is confirmed by Mandel test at 0.05 significance level ($F^* < F_{0.05,1,3}$). These results confirm the effectiveness of the LVD method in achieving homogeneous distribution and a proportional response in the XRD signal, even in a complex organic matrix. Furthermore, the high sensitivity implied by the steep slope suggests the method's potential for detecting even minor mass fractions: according to Eurachem [40], a first estimation of the limit of quantification (LOQ) from the calibration line is 0.06% (w/w) of quartz. Since the mass fraction regulatory limit is set at 0.1% for RCS, recovery tests were performed in a close region, by measuring in triplicate two samples obtained by spiking S1 with 0.11% and 0.14% of quartz. The resulting recovery values were not significantly different from 100% ($104 \pm 8\%$ and $96 \pm 6\%$), respectively, where the uncertainty was calculated by taking into account the quartz crystallinity, the calibration uncertainty and the standard deviation of the triplicate measurements [41]. For the sake of completeness, the recovery was also calculated for a mass fraction closer to the middle of the investigated range (0.98%), where the calibration uncertainty is at minimum. A sample spiked with 0.78% of quartz provided a recovery value of $(95 \pm 4)\%$.

After the first characterization, the original unspiked S1 sample diffraction pattern was collected with the low-power benchtop D2 diffractometer to assess its suitability for the task. Despite a slightly more pronounced SDE and peak width, which were expected due to the smaller goniometer radius with respect to

Explorer (141 mm vs. 240 mm), larger Soller slits and detector active area, the angular resolution and diffraction signal intensity were fine, as can be seen in Figure 5, where the comparison between Explorer and D2 is reported.

The absolute counts are larger for D2, mainly as a consequence of the larger detector active region and Soller slits. By normalizing both diffraction patterns with respect to the maximum intensity, i.e., the corundum (104) peak (Figure 5b–d), it is possible to appreciate the resemblance between the outcomes of the two instruments. Thus, both the high and low-power instruments are compliant with the angular resolution and peak position accuracy needs for the detection of crystalline quartz.

3.3 | Initial Estimation of Crystalline Silica

In the previous section, the linear response of the quartz signal as a function of its mass fraction was assessed in a range up to 2.5%, providing a calibration for the analysis of unknown samples. However, any departure of their matrix composition from the investigated one may affect the accuracy of the estimation, which is already characterized by a larger uncertainty at the edges of the calibration curve. Thus, a versatile quantitative approach, tailored to each unknown sample and more focused on a limited range close to the expected value, was selected: the standard additions method (EN 17289). In order to establish the range, a first estimation of the expected value must be first provided. Thus, sample S1 spiked with 0.073% of quartz was investigated as a positive test sample, in order to evaluate the possible bias of the proposed method. For an initial estimation of the CS content, two established normative methods, as referenced by EN 17289, were employed: the Rietveld refinement method and the RIR single peak method. For both approaches, ZnO was chosen as the internal standard due to its well-defined diffraction pattern, limited overlapping with the reflections of interest and chemical inertness within the sample matrix. Its characteristic reflections at approximately $2\theta = 31.76^\circ$ (100), $2\theta = 34.42^\circ$ (002), and $2\theta = 36.25^\circ$ (101) provide clear and distinct peaks for quantification. Figure 6a illustrates a representative diffractogram following the addition of the ZnO internal standard (6.24%), clearly showing the region for quartz and ZnO main peaks, whose single-ROI acquisitions are reported in Figure 6b,c, respectively.

The Rietveld method offers a comprehensive approach to quantitative phase analysis by fitting the entire acquired diffraction pattern, allowing handling of complex mixtures and peak overlaps, accounting for various instrumental and structural parameters, thus providing more accurate results. In order to collect an adequate number of reflections and to discriminate the small quartz (101) peak, a diffractogram was collected in continuous scan mode from $2\theta = 15^\circ$ to $2\theta = 75^\circ$ at $1^\circ/\text{min}$, thus requiring about 1 h (Figure 6a). The collected data were then processed with the Rietveld algorithm of Profex: in principle, for each identified phase a description of its structure is required to proceed with the parameter refinement and full profile fit. The paraffinic matrix, which is only partially crystalline, has no suitable structural information available: fortunately, its few crystalline peaks and amorphous hump are distinguishable from corundum, quartz, and zincite

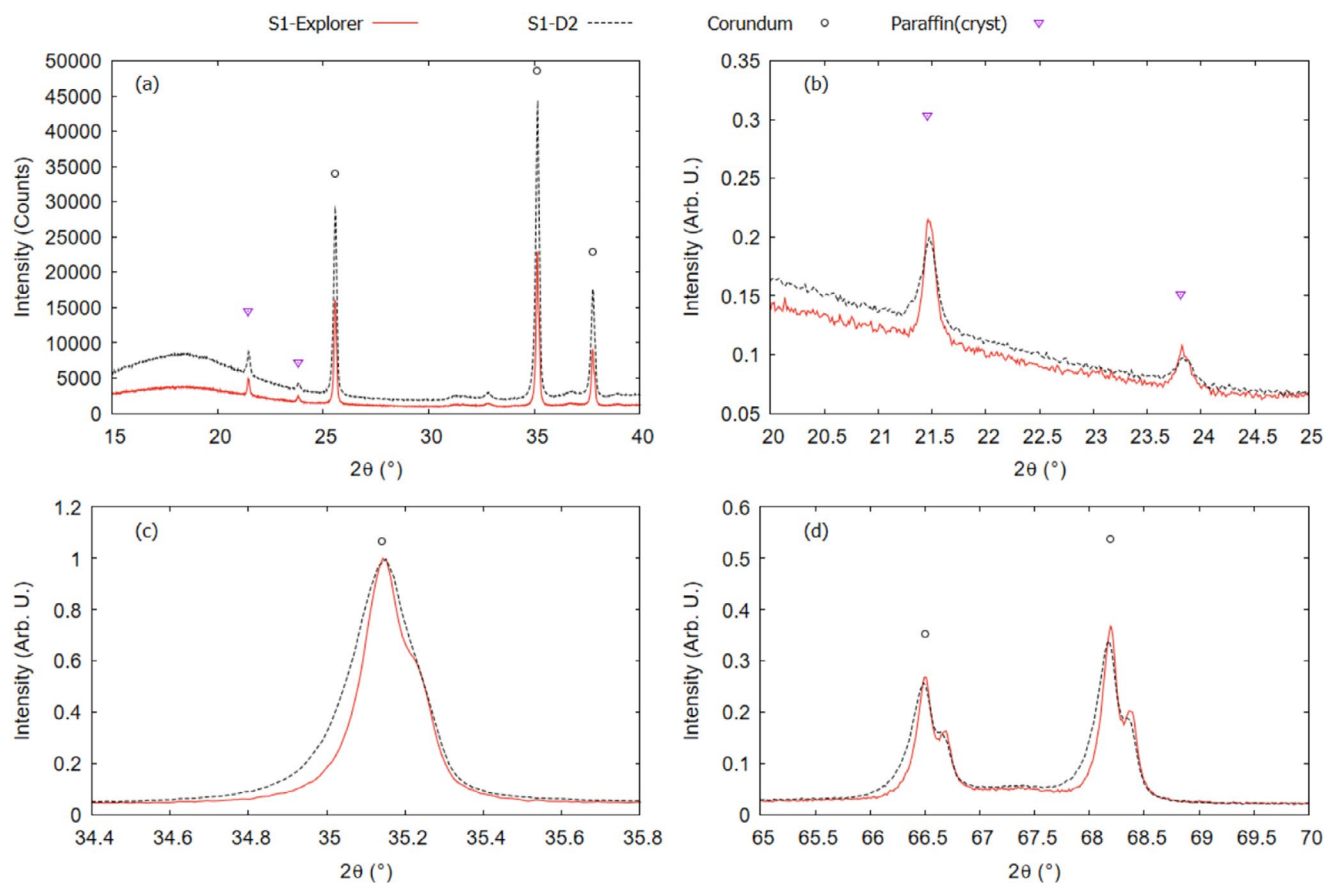


FIGURE 5 | Comparison of the diffraction pattern of sample S1 collected with Explorer (red) and D2 (black dashed) diffractometers. (a): Absolute intensity values; pattern normalized with respect to corundum (104) peak in the region of paraffin peaks (b), corundum (104) (c), and corundum (214) and (300) (d). The different angular resolution is apparent, as the similar peak-to-background ratio. Patterns were corrected for SDE. [Colour figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

peaks, thus allowing the discarding of it and proceeding with the fit and quantification of the crystalline phases relative to the known zincite internal standard. The quantitative results were: $(31.35 \pm 0.17)\%$ for corundum, $(0.071 \pm 0.012)\%$ for quartz, and $(68.58 \pm 0.17)\%$ for the remaining phases (paraffin and potentially undetected phases). Interestingly, the result for quartz is close to the nominal value $(0.073 \pm 0.002)\%$; the relative uncertainty of the estimation, 17%, is mainly due to the small quartz signal.

In scenarios where time of analysis is a critical factor, the RIR single peak method offers a faster alternative. Instead of recording a large 2θ range, this method focuses on scanning only the regions of the primary reflections of quartz (101) and ZnO (101), with a total measurement time of 20 min (Figure 6b,c). The intensity ratio of these selected peaks and their relative scattering factors (I/I_C) values, tabulated in the available databases, are then used for quantification. Despite its poor accuracy with respect to a full-profile method, RIR is effective in providing an initial fair estimation $(0.098 \pm 0.010)\%$ for the following quantification with the standard addition method. The Rietveld and RIR estimations provided consistent results for the initial estimation of CS content, as depicted in Figure 6d. The consistency between these two methods, despite their differing data acquisition and analysis approaches, further proves the effectiveness of the LVD pretreatment.

Beyond quartz, this method holds potential for the quantification of other crystalline silica polymorphs, notably cristobalite. The proximity and possible overlap of the crystalline paraffin reflections with the primary peak of cristobalite, which typically appears at approximately $2\theta = 21.95^\circ$ (101), might lead to misinterpretation.

Thus, sample S1 was spiked with a known amount, 0.097%, of cristobalite (SRM 1879b) to assess the capability of the diffractometers to distinguish its main peak, whenever it might be present. Figure 7 reports the diffraction patterns collected with Explorer of sample S1 with and without the cristobalite spike: it is apparent that the angular resolution achieved with the described setup is sufficient to discriminate between the primary peaks of cristobalite and any potential interfering peaks from organic components, such as paraffin, that might be present in the paste matrix. According to Section 3.2 and Figure 5a, D2 qualifies as well. As mentioned, these results are a promising starting point for the possible evaluation of the outlined approach for cristobalite too.

In case secondary peaks of quartz ($2\theta = 20.85^\circ$) or cristobalite ($2\theta = 31.49^\circ$) are required, e.g., for possible interfering phase check according to EN 17289-1 and ISO 24095, two additional ROIs must be collected with an extended counting time because of their lower scattering factor with respect to primary peaks.

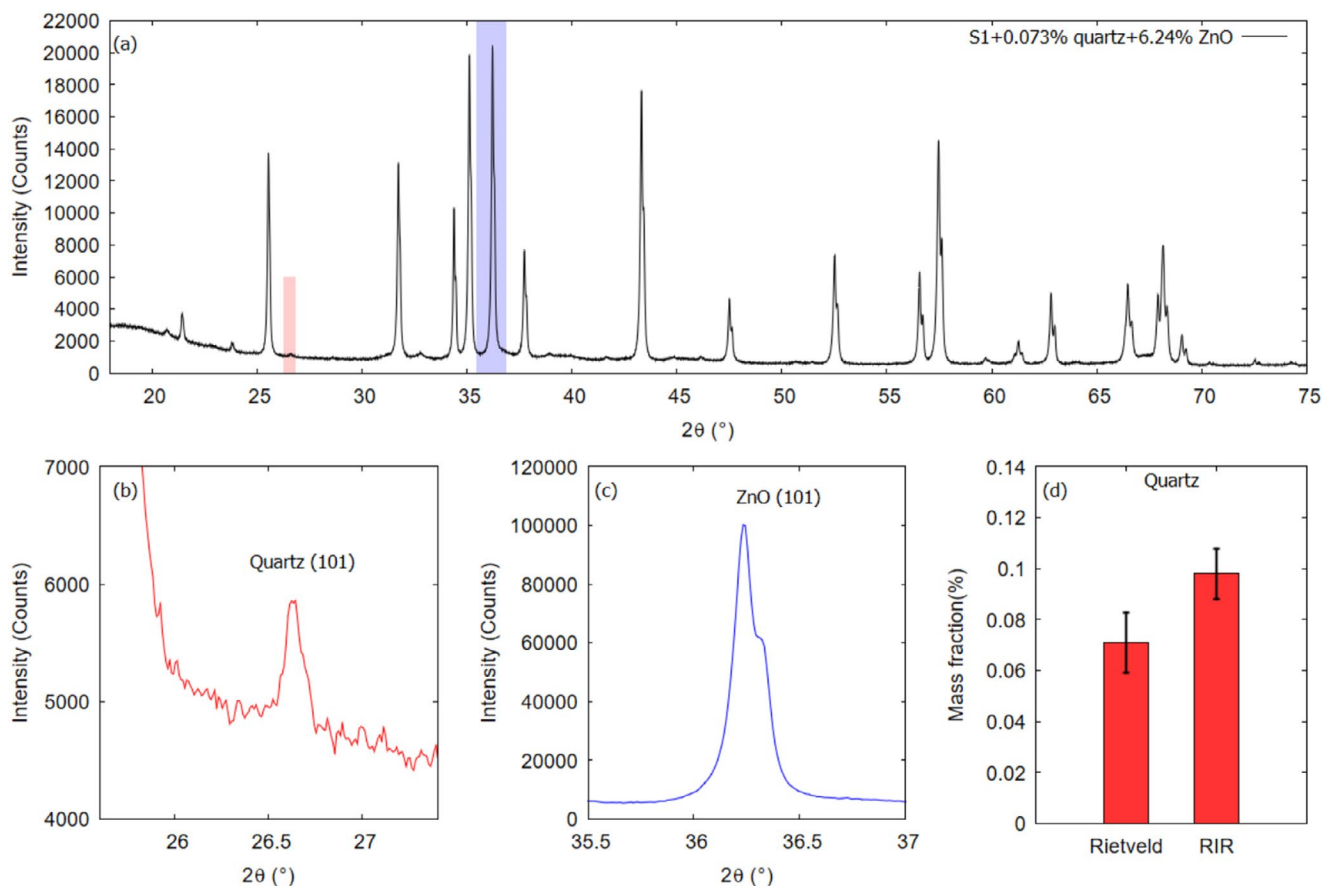


FIGURE 6 | Diffraction pattern for sample S1 spiked with quartz at 0.073% and zincite as internal standard (a). The shaded rectangles highlight the region of interest for the single peak acquisitions for quartz (101) (b) and ZnO (101) (c), both collected with an increased counting time with respect to (a); results of the first quantitative analysis of quartz with both Rietveld and RIR method (d). Measurements were performed with Explorer. [Colour figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

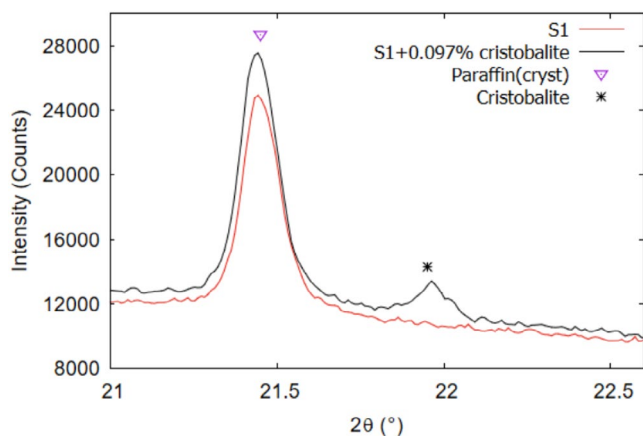


FIGURE 7 | Diffraction pattern of sample S1 before (red) and after (black) spiking with cristobalite. [Colour figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com)]

3.4 | Application of the Standard Addition Method With LVD

Once a first estimation (w_c) of the quartz mass fraction is available, it is possible to proceed with the method of standard additions (Section 4 in S1) for a more accurate analysis, according

to EN 17289-1. Sample S1 with 0.073% of quartz was spiked with amounts of quartz following the LVD method outlined in Section 2.2 for each of them. In the end, four different S1 portions with different quartz content were available for deposition in the sample holder. The crystallinity of the added quartz is considered either from the beginning or after the analysis. Figure 8a shows the increase of quartz (101) peak with the spiking level: it is possible to see that, despite the large and variable background, the peaks are clearly distinguishable and grow with the spiking level. Each spiked S1 portion was deposited in three different sample holders and measured.

The average values and their standard deviations were used for a weighted linear regression (WLR) versus the added quartz mass fraction (Figure 8d). The resulting slope and intercept are reported in Table 2: the intercept with the x -axis (Equation 22 in S1) provides an estimated quartz mass fraction of $(0.071 \pm 0.004)\%$, which is close to the nominal one, i.e. $(0.073 \pm 0.002)\%$. Linearity is confirmed by the cumulative probability function for χ^2 [42] and Lack of Fit test (ISO 11095) (Section 5 in S1).

The method was finally applied to two pastes with similar paraffin matrix and corundum abrasive powder, S2 and S3, for which a tiny (101) quartz peak was present. The measurements were performed with D2 diffractometer, to substantiate further the suitability of low-power diffractometers to the task of crystalline

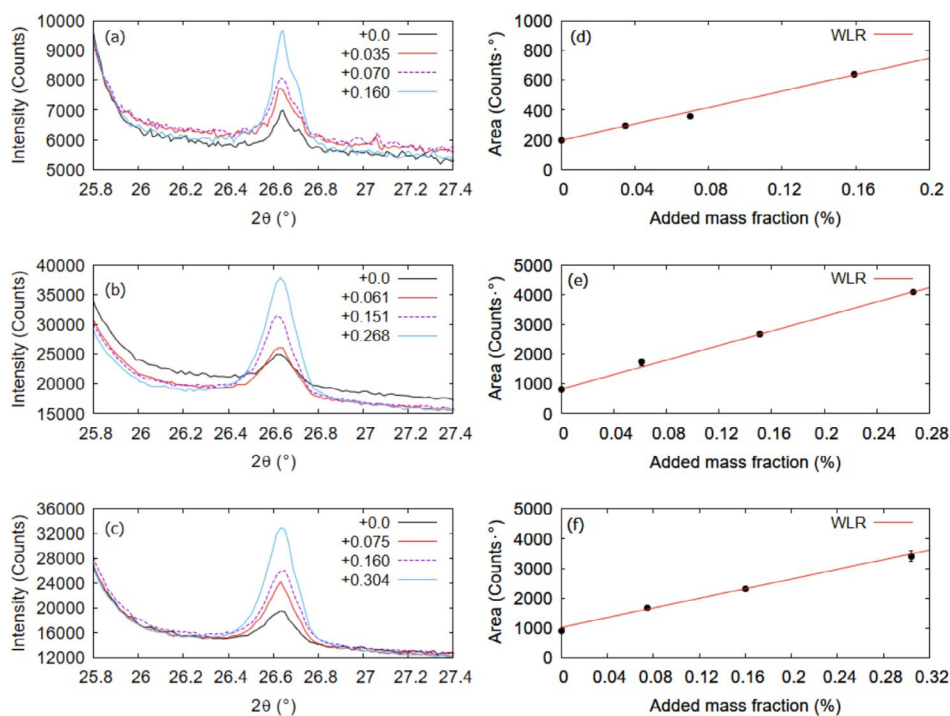


FIGURE 8 | Quartz (101) peaks at different standard addition values for spiked (0.073%) S1 (a), S2 (b), and S3 (c). Weighted linear regression (WLR) of quartz (101) peak area versus the quartz mass fraction for spiked S1 (d), S2 (e), and S3 (f). [Colour figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/xrs.70128)]

TABLE 2 | Results of the least squares for the standard additions procedure for single (from a to f) and averaged (av) spiked values.

Sample		Slope (counts°/%)	Intercept (counts°)	R^2	$P(\chi^2 > \chi_{\min}^2)$	Lack of fit mandel test $P(F > F_{\text{calc}})$	Mass fraction (%)
S1	av	2765 ± 92	196 ± 5	0.9978	0.015	0.07	0.071 ± 0.004
S2	av	12221 ± 172	822 ± 17	0.9996	0.28	0.21	0.059 ± 0.003
	a	11900 ± 291	801 ± 45	0.9988	—	0.72	0.059 ± 0.005
	b	12113 ± 348	872 ± 54	0.9984	—	0.51	0.063 ± 0.006
	c	11918 ± 895	1000 ± 140	0.9888	—	0.50	0.073 ± 0.015
S3	av	8117 ± 649	1022 ± 81	0.9874	0.05	0.42	0.109 ± 0.017
	d	9324 ± 711	880 ± 125	0.9885	—	0.95	0.082 ± 0.017
	e	7582 ± 780	996 ± 137	0.9792	—	0.12	0.124 ± 0.010
	f	7467 ± 262	1068 ± 46	0.9975	—	0.27	0.114 ± 0.026

quartz detection. The first quantitative estimation was carried out with the RIR method, as outlined in Section 3.3, providing 0.122% and 0.153% for S2 and S3, respectively. Then, based on these results, the standard addition method was performed (Figure 8b,c) by taking an aliquot from each spiked sample and measuring it (single series). The last two steps were repeated to have three single series of incremental spiking level, to evaluate the repeatability of their estimations. In fact, for the sake of analysis time minimization, the procedure might not be always performed in triplicate in the lab, thus an assessment of the spread of the results for single measurements in comparison with the averaged ones (Figure 8e,f) may be useful. Both single and averaged measurement results for S2 and S3 are reported in Table 2, where the uncertainty for mass fraction is calculated according to Eurachem [41]. The linearity of the model is

substantiated by the cumulative probability function for χ^2 and lack of fit test for the regression with repeated measurement spikes, while by the Mandel test for the regression of single measurement spikes ($p > 0.05$). The single measurement results are compatible with each other and the average measurement values, considering their uncertainty. Moreover, for sample average (av) S3 the relative uncertainty is larger (16%) than the other two (6% and 5%). The compliance with a set limit value, e.g., 0.1%, can be assessed through the implementation of decision rules and acceptance levels determined through guard bands, based on the expanded uncertainties of the results, according to Williams and Magnusson [43]. With the aim of maximizing the confidence of correct acceptance, the decision rule may state that there should be at least a 95% probability that the value of the measurand is less than the limit. For instance, the average

S1 and S2 have an acceptance limit set at about 0.09%, given by the difference between the upper permitted limit (0.1%) and the guard band (0.01%), which makes the results compliant. On the other hand, S3 is clearly non-compliant, being larger than 0.1%. The compliance dependence on measurement uncertainty calls for the establishment of a target value of the latter, which could be calculated by setting the maximum mass fraction deemed acceptable for the sample to be declared compliant [44]. This is important for minimizing the risk of wrong rejection for values just below the set limit. Considering the type of matrix and the threshold level at 0.1%, a target relative uncertainty up to 10%, resulting in a maximum acceptance limit of 0.077%, may be sound at this stage of the methodology [15]. In case the measurement uncertainty is larger than the target value, it may be reduced with additional replicate measurements and, possibly, a material for spiking with a smaller crystallinity uncertainty, e.g., NIST 1878. Of course, the trade-off between the cost of the measurements and the cost of wrong decisions must be evaluated when establishing target uncertainty values [44].

In view of the method optimization, in case of D2 the acquisition time may be reduced by either limiting the size of the scanning region or performing a static measurement as for Explorer, to have signal from the peak of interest for the whole measurement time.

It is worth pointing out that the quantifications performed with each instrument relied on the quartz and ZnO peak-area ratio and the standard additions approach, thus no absolute intensities were compared across the two systems, nor calibrations were used. Importantly, the dual-instrument dataset is intended to demonstrate method transferability rather than a bias-free inter-instrument comparison.

4 | Conclusions

This work presents a pragmatic analytical approach to determine quartz, the most common crystalline silica polymorph, in paraffin-rich and corundum-bearing polishing pastes by XRD. The focus is on all crystalline quartz size fractions in these pastes, because under some work processes larger size fractions may be converted in the harmful respirable one. The promising outcomes pave the way for the potential applicability of standards, e.g., EN 17289, EN 13925, to these complex, viscous and partially amorphous organic matrices. The sample preparation method, optimized to homogenize crystalline powders within a reduced viscosity matrix, allowed to realize a calibration curve for quartz spikes and assess its linearity, providing quantification capabilities below 0.1% for crystalline quartz mass fraction, thus complying with the EU REGULATION (EC) No. 1272/2008 for estimations below the set limit. Moreover, the application of the internal standard method and standard additions to one known spiked sample showed a negligible bias in the quantification, which was thus performed for two similar pastes having tiny quartz peaks in their diffractograms. The repeatability of measurements and the linearity of linear regressions proved the effectiveness of the proposed analytical approach, which can be further refined and validated in the framework of inter-laboratory comparisons.

With the aim of making the proposed approach as convenient as possible for laboratories, commercially available powders were characterized by means of certified reference materials from NIST, to use them as internal standards (zincite) or spikes (quartz), without the need of necessarily depending on supplies of scarce certified reference materials. Similarly, both floor-standing and benchtop diffractometers from two different manufacturers were assessed, to consider the variability in instrumentation settings and possibly tune them with the aim of reaching the required detection capabilities for crystalline silica.

The potential of the method for the other main crystalline silica polymorph, cristobalite, was checked briefly by showing its capability to detect it at levels below 0.1% (w/w) in this kind of matrices. Being the cristobalite and quartz scattering factors quite similar, the same spiking procedures outlined in this study might be tested for the former in future, when a suitable and commercially available cristobalite powder is identified and characterized, as done for quartz and zincite.

In addition to inter-laboratory comparisons, the envisaged developments of this work may focus on the possible separation of the organic matrix from the mineral powders by means of organic solvents to concentrate the latter. Then, particle sedimentation procedures may be attempted to determine the size-weighted fine fraction of crystalline silica according to EN17289-3, in order to have the actual RCS fraction. However, a *silica-free* approach should be pursued because particle size reduction may occur during processing of materials, thus increasing the chance of a respirable fraction larger than previously estimated. Moreover, the possible extension of the proposed methodology to other industrial products consisting of similar complex organic matrices should be investigated in the light of increasing attention to both occupational health risks and high-quality products.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section. **Figure SM-1:** (A) Simplified visualization of the inflammatory diseases and the silicosis caused by the exposure to RCS and (B) the main sectors involved in silica market inspired by the data reported in silica market (2024), ID: GVR-3-68038-064-4, <https://www.grandviewresearch.com/industry-analysis/silica-market> (consulted the 22/11/2025 at 3.00 p.m.). **Table SM-1:** xrs70128-sup-0001-Supinfo.docx. **Table SM-2:** xrs70128-sup-0001-Supinfo.docx.