

Online Quantitative Analysis of Chlorine Contents in Chlorinated Paraffins by Facile Raman Spectroscopy

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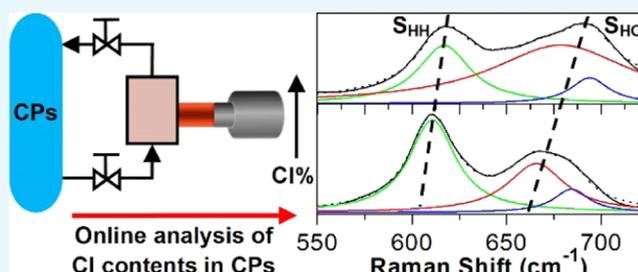
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ABSTRACT: Online analysis of industrial chemicals is extremely important for managing product quality and performance. The chlorine (Cl) content is one of the most important technical metrics for chlorinated paraffins (CPs), and the conventional approaches to estimate Cl contents require transforming the Cl element to chloride followed by quantitative analysis with either titration or instrumentation, which are normally tedious and time-consuming and cannot simultaneously guide the industrial production. Here, we developed a rapid, real-time, and online approach to determine the Cl content of CPs with facile Raman spectroscopy. The chlorination of paraffins generated two new Raman peaks at 610–618 and 668–690 cm^{-1} , which are associated with the vibrational modes of the S_{HH} and S_{HC} conformations of the C–Cl bond in CPs, respectively. More importantly, the corresponding peak of the S_{HH} conformation decreased and that of the S_{HC} conformation increased with the enhancement of the chlorination degree of CPs. The ratiometric calculation of the two respective Raman peak areas leads to a quantitative analysis of the Cl content of CPs. The developed approach can online provide the Cl contents of CPs within seconds accurately but without the tedious sample treatment required by conventional approaches. The strategy of integrating Raman analysis with the industrial pipeline will help in managing the production and quality control of industrial chemicals.



INTRODUCTION

Industrial chemicals exist in many aspects of our daily life. The monitoring or detection of key information on chemicals is essential to optimize the production process and guarantee the quality of commonly available commodities. Integration of the analysis technique with industrial processing is thus extremely important to achieve this goal. As one of the important industrial chemicals, chlorinated paraffins (CPs) have been widely used as plasticizers, flame retardants, and lubricant additives.^{1–3} The production of CPs is normally conducted through the radical chlorination of paraffins under ultraviolet light or heating, generating a large and complex class of chemical mixtures. The chlorine (Cl) content of CPs is one of the most important technical metrics to control the properties and performances of the final products.^{4,5} The Cl content of CPs is usually measured with a wealth of established techniques,^{4,6–9} such as the mercurimetric method, ion chromatography, and mass spectrometry. In general, these techniques require tedious sample pretreatment steps, including degassing-free Cl_2 and HCl from samples, transforming the Cl element into Cl^- by either oxygen flask combustion or high-temperature pyrolysis, and measuring the Cl^- concentrations with either titration or instrumental analysis (Scheme 1A). Incomplete degassing or insufficient sample decomposition results in inaccurate Cl content

measurement. Moreover, these complicated analysis approaches cannot online measure the Cl contents quantitatively. Therefore, a simple, rapid, and real-time assay is highly desirable to monitor the chlorination degree and manage product quality in practical scenarios.

The production of new chemicals in an industrial pipeline normally involves chemical structural changes. Conventional spectroscopic techniques (e.g., near-infrared spectrum, Raman spectrum) have been widely utilized to investigate the changes of the structure and conformation of chemicals.^{10–16} For example, the isomers existing in mixtures of alkyl chlorides have been easily differentiated by measuring their vibrational frequencies with infrared spectroscopy.¹⁵ The C–Cl stretching region of the Raman spectrum of poly(vinyl chloride) has been shown to be particularly sensitive to the conformation of the polymer chains.¹⁶ The existing Cl in liquid CP is a typical secondary chloride with both S_{HH} and S_{HC} conformations based on Mizushima's notation,^{16–18} representing the C–Cl

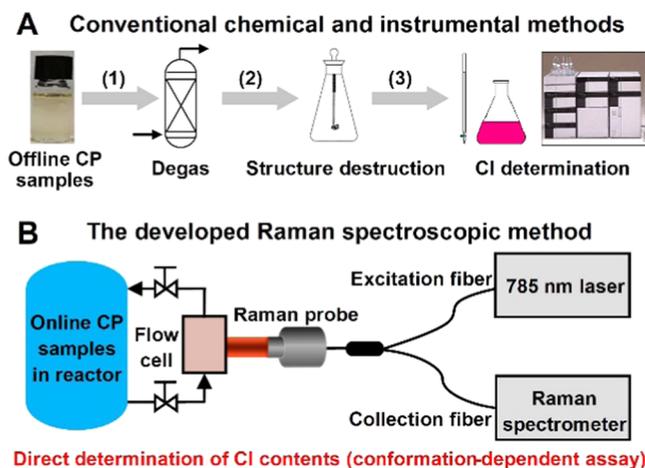
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Scheme 1. (A) Conventional Chemical and Instrumental Methods and (B) the Developed Raman Spectroscopic Method for the Quantitative Determination of Cl Contents in CPs



stretching mode of the CH–Cl units in syndiotactic and isotactic sequences, respectively. The investigation of chlorinated polyethylenes showed that chlorination can affect the structure and conformation of CPs, which, in turn, can be used for the quantitative determination of Cl contents in CPs by the corresponding vibrational frequencies with specific conformations.^{19,20} In addition to the rapid and nondestructive data acquisition process, Raman spectroscopy has great potential for the online monitoring of chemical productions.^{21–24}

In this regard, we developed a facile method for the online determination of the Cl contents in liquid CPs utilizing the Raman technique. The conformational content of the C–Cl stretching mode transformed from S_{HH} to S_{HC} with increasing the chlorination degree of CPs, and the corresponding area ratio of S_{HC} conformation in the Raman spectrum to that of the S_{HH} mode is proportional to the Cl content of CPs. Implemented with the aid of a quartz flow cell accessory, the Raman spectra of the online CP samples in reactors could be obtained within seconds with a portable and integrated Raman device (Scheme 1B). It is worth noting that the conformation-dependent assay of the Cl contents does not require degassing and destructive treatments of CP products, which is favorable for the rapid, real-time, and online determination of Cl contents in practical CP samples.

EXPERIMENTAL SECTION

Materials. Paraffins were obtained from Nanjing Jinling Petroleum and Chemical Co., Ltd. CP standard samples with various Cl contents (e.g., 42.00, 46.00, 50.00, 54.00, and 58.00%) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. Two types of industrial CP samples were gifted from Anhui Xingxin Material Technology Co., Ltd. The semi-CP samples were degassed after being collected from the reactor. The online CP samples were directly collected from the reactor without any degassing or other treatments. It was noted that the above CP standard samples and industrial CP samples had the same carbon chain length ranging from C_{14} to C_{17} . All other reagents were of analytical grade unless stated.

Standard Mercurimetric Method for the Determination of Cl Contents in CPs. The reference values of Cl contents in CP samples were determined by a standard

mercurimetric method.²⁵ The collected CP samples were first wrapped with filter paper and placed on the platinum wire of the oxygen combustion bottle. Then, the samples were burned in an oxygen bottle. The combustion of CPs turned the Cl atom to chloride followed by full adsorption with 20 mL of 0.18 M KOH. Before the titration experiments, the solution was adjusted to be slightly acidic by the addition of HNO_3 (using 0.1% bromophenol blue as an indicator, the color of the solution changed from blue to yellow). One milliliter of 0.5% of diphenylcarbazone ethanol solution was added to the test solution, and 0.025 M of $Hg(NO_3)_2$ standard solution was added until the color of the solution changed from yellow to purple. Finally, the Cl contents were calculated from the amounts of the consumed titrant.

Raman Spectroscopy for Quantitative Analysis of Cl Contents in CPs. Raman spectra of paraffin and CP samples were recorded with the BWS465-785S system (B&WTEK) equipped with a 785 nm excitation laser and a charge-coupled device detector. The laser and spectrometer were fiber-coupled to the Raman probe. The Raman spectra of liquid CPs were directly recorded with a Raman spectrometer with an excitation intensity of 300 mW and an integration time of 8000 ms. To measure the online CP sample, the Raman spectrometer was integrated with a pipeline with a flow cell accessory and the sample spectra were recorded with the same setup condition. In view of the existing S_{HH} and S_{HC} conformations in CPs, the obtained Raman spectra were regarded as a sum of several Lorentzian peaks corresponding with various conformations of the C–Cl bond. The Raman spectra were further fitted to a Lorentzian mixture model, and one and two major peaks were used for the respective S_{HH} and S_{HC} conformations. The spectral area ratios of the S_{HC} region to that of S_{HH} were then utilized to determine the Cl contents of CPs. Each sample was measured in triplicate, and the average was presented.

RESULTS AND DISCUSSION

Characteristic Raman Frequencies of Paraffin and CP Molecules. We first measured the Raman spectra of paraffin and CP with a portable Raman device. The chlorination of paraffins was associated with the replacement of the C–H bond with the C–Cl bond in methyl/methylene groups. As a result, the Raman peaks for the longitudinal acoustic modes (LAMs)^{26,27} of a planar zigzag carbon backbone at 220 and 401 cm^{-1} disappeared, and the corresponding Raman peaks for $\delta(C-C-Cl)$ at 286 and 357 cm^{-1} and $\nu(C-Cl)$ at 612 and 681 cm^{-1} appeared (Figure 1). The intense bands at 612 and 681 cm^{-1} result from the vibrational modes of the S_{HH} and S_{HC} conformations in CP syndiotactic and isotactic sequences.^{16,28} In addition, the positions and intensities of the peaks for $\rho(CH_2)$ at 844–889 cm^{-1} , $\nu(C-C)$ at 1063–1132 cm^{-1} , $\tau(CH_2)$ at 1301 cm^{-1} , $\delta(CH_2)$ at 1438 cm^{-1} , and $\nu(CH_2)$ at 2852 cm^{-1} changed due to the substitution of the hydrogen atoms with the Cl ones (see the detailed assignments of the main peaks in Table S1). The significant Raman spectral variation upon chlorination of paraffin indicates that the Raman approach is able to differentiate the composition and structure of paraffins and their chlorinated products with unique spectroscopic fingerprints.

Correlation of Chlorination Degree with Raman Frequencies of CPs. To check the possibility of quantitative analysis of the chlorination of CPs, we further examined the Raman spectra of CP standard samples with different degrees

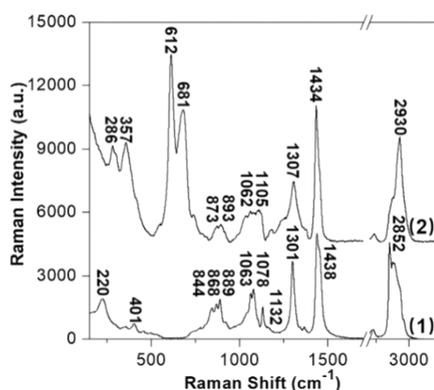


Figure 1. Raman spectra of liquid (1) paraffin and (2) CP molecules.

of chlorination degrees. The detailed Raman fingerprint of CPs is shown in Figure 2A. Specifically, the Raman intensity of the S_{HH} vibration ($610\text{--}618\text{ cm}^{-1}$) of the C–Cl bond decreases and that of the S_{HC} vibration ($668\text{--}690\text{ cm}^{-1}$) increases gradually with an increasing chlorination degree from 42.00 to 58.00%. This observation is consistent with the previously reported conformational change from S_{HH} to S_{HC} for chlorinated polyethylene.²⁰ It is noted that the frequency of the S_{HH} conformation blue-shifted from 610 to 618 cm^{-1} and that of S_{HC} blue-shifted from 668 to 690 cm^{-1} (Table S2), as the chlorination degree increases from 42.00 to 58.00%, which might be attributed to the presence of longer chlorinated segments and the enhancement of the heterotactic mode of chlorination in the CP chains.^{18,21} The peaks for the S_{HH} and S_{HC} conformations were processed and fitted using Lorentzian profiles (Figure 2B). The corresponding peak area was calculated with the fitting curve, and the ratio of S_{HC} to S_{HH} , $A(S_{HC})/A(S_{HH})$, exhibits a linear correlation with Cl contents in the range of 42.00–58.00% ($R^2 = 0.9950$; Figure 2C). It is noted that the CPs used in this study have carbon chain lengths ranging from C_{14} to C_{17} . The intensity ratios of S_{HC} to S_{HH} would be different for materials with the same Cl content but much larger molecular weights than those of CPs (e.g., chlorinated high molecular mass polyethylene).²⁰ A more detailed analysis is required to understand the relationship

between the molecular weight fractions and Cl content. As such, Raman spectroscopy is able to quantitatively evaluate the Cl contents of CPs with a fixed carbon chain range.

Determination of Cl Contents in Semi-CP Samples.

The reliability and practicality of the Raman spectroscopic method were further estimated with real CP samples. Five semi-CP samples were first assayed by a portable Raman device. The obvious vibrational change of Raman spectra upon chlorination is shown in Figure S1. The corresponding Cl contents of each sample were further estimated with the developed quantitative Raman approach (Table 1). The

Table 1. Cl Contents in the Semi-CP Samples

sample no.	referenced method (%) ^a	developed method (%) ^b	relative error (%)
1	46.29	45.80	−1.06
2	47.89	48.82	1.94
3	49.28	49.50	0.45
4	51.63	50.89	−1.43
5	55.19	54.69	−0.91

^aThe data represent Cl contents in the five semi-CP samples determined by the standard mercurimetric method. ^bThe data represent Cl contents in the same samples determined by the Raman spectroscopic method. Each sample was done in triplicate, and the average was presented.

obtained Cl contents in these samples are comparable with that from the traditional mercurimetric method, demonstrating the reliability of the Raman method for estimating Cl contents. Noteworthy is that it required highly toxic titrants and took several hours to obtain the final results for the traditional approach resulting from tedious processes including combustion/pyrolysis and titration. Meanwhile, the developed Raman approach provides Cl contents within seconds. These results indicate that the developed Raman spectroscopic method is robust in measuring the Cl contents in real CP products.

Determination of Cl Contents in Online CP Samples.

In view of the facile operation of the Raman measurement, we further tested the feasibility of utilizing it for online monitoring of CP production in an industrial reactor. In practice, CPs are synthesized by a typical continuous production process (Figure

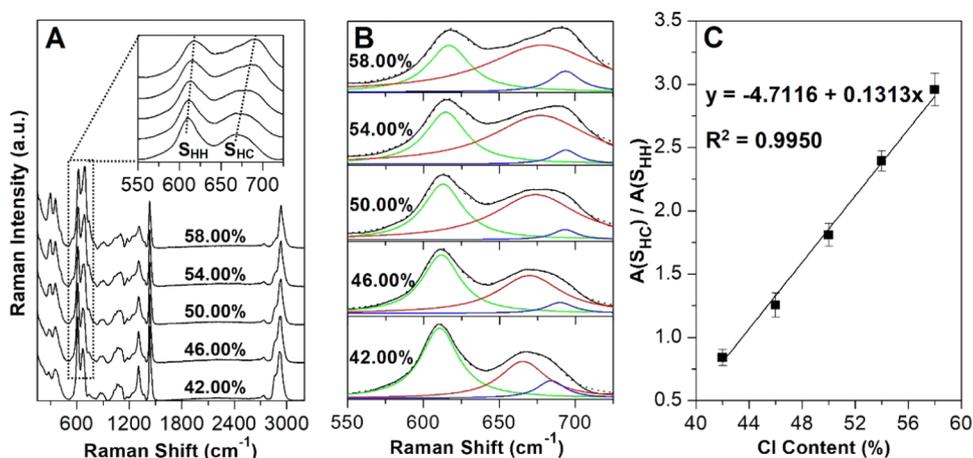


Figure 2. (A) Raman spectra of CP standard samples with 42.00, 46.00, 50.00, 54.00, and 58.00% Cl (the inset is the magnification of the C–Cl stretching region). (B) The Lorentzian fitting of the Raman spectra of CP standard samples in the range of 550–725 cm^{-1} (the black solid and dotted lines represent the experimental and fitted intensities, respectively; the green, red, and blue lines show the corresponding Lorentzian peaks). (C) The linear correlation of the Raman peak area ratio of S_{HC} to S_{HH} with the Cl content was from 42.00 to 58.00%.

3A). The paraffins first flowed into reactor 1 and reacted with Cl_2 under the catalysis of light, and then the obtained materials

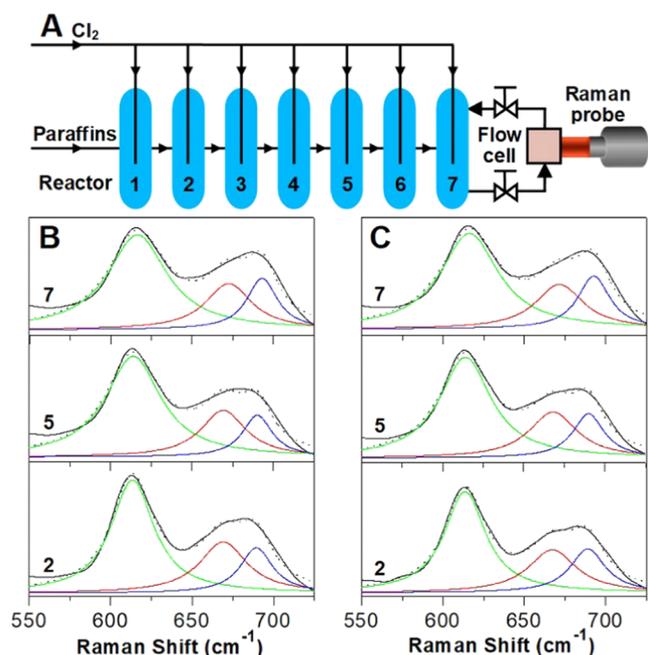


Figure 3. (A) The typical continuous production process for CPs with seven reactors in series and online spectral measurements by integrating the Raman probe with the reactor through a flow cell accessory. The Lorentzian fitting of the Raman spectra of the three online CP samples (B) without and (C) with degassing treatment.

automatically overflowed to reactor 2 and continued the chlorination process. Repeating this operation across several reactors generated the final CP product. The Raman spectra of samples could be easily measured by coupling the Raman spectrometer with any reactor through a flow cell accessory (Figure 3A). We conducted Raman measurement of online CP samples in three different reactors (2, 5, and 7) with the coupled flow cell accessories. The respective Raman spectra showed strong vibrational frequencies of S_{HC} and S_{HH} (Figure 3B). In addition, we collected the respective samples from these three reactors, followed by degassing treatment, and measured their Raman spectra (Figure 3C). The Cl contents in the online undegassing CP samples are 44.99, 48.11, and 51.49%, which are statistically close to those degassing samples (Table 2). The results demonstrate that the free Cl-containing species existing inside online samples (e.g., residual Cl_2 and HCl) have an unignorable effect on the analysis of Cl contents.

Table 2. Cl Contents in Online CP Samples

sample no.	referenced method (%) ^a	developed method (%) ^b			
		undegassed	relative error	degassed	relative error
1	44.83	44.99	0.36	45.37	1.20
2	47.67	48.11	0.92	47.42	-0.52
3	51.14	51.49	0.68	52.16	1.99

^aThe data represent Cl contents in the three online degassing CP samples determined by the standard mercurimetric method. ^bThe data represent Cl contents in the three online undegassing and degassing CP samples determined by the Raman spectroscopic method.

This is because the free Cl-containing species are not involving the conformational variations of CPs. Moreover, these online samples with and without degassing treatment were further evaluated by the standard mercurimetric method. The results from the degassing samples are similar to those measured with the Raman method. These low errors between the standard method and the developed Raman approach illustrate the reliability of the Raman approach for measuring the Cl content in both semi-CP and online CP samples. It is worth noting that the relative errors calculated by the mercurimetric method are more than 10% for the undegassed samples as compared to those of degassed samples (Table S3). These comparisons demonstrate that the conformation-dependent Raman assays without the need for degassing and destructive treatments are favorable for the rapid, real-time, and online determination of Cl contents in CP samples.

CONCLUSIONS

In summary, we developed a novel, rapid, and online Raman spectroscopic strategy to determine the Cl contents in CPs based on the specific Raman frequencies correlated with the conformation of chemical bonds. The chlorination degree has a distinctive effect on the Raman peak area ratios of the C–Cl stretching frequencies of S_{HC} to S_{HH} . The ratiometric calculation of Raman peak areas enables the conveniently quantitative measurement of Cl contents in both semiproducts and online samples with high accuracy. Without the complicated degassing and destructive treatments in traditional methods, the conformation-dependent Raman assay can directly guide the production of CPs with a portable or integrated Raman device. The Raman spectroscopic method offers a robust approach to managing the quality control of Cl contents in organic chlorides as well as other industrial chemicals.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c06674>.

Raman peak assignments of paraffins and CPs, frequencies of S_{HH} and S_{HC} conformations in CPs with different chlorination degrees, quantitative analysis of Cl contents in semi-CP samples, and relative errors between the online CP samples with and without degassing treatments by the mercurimetric method (PDF)

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Notes

The authors declare no competing financial interest.

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