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Non-invasive investigation of liquid materials using energy dispersive X-ray scattering

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ABSTRACT

Application of the energy dispersive X-ray scattering (EDXRS) for the identification of pure liquid materials was reported for the first time. Three liquid systems of primary alcohols, benzene homologues and chloromethanes were carefully probed and the scattering spectra were described. On the basis of the different structures and compositions of these compounds, the scattering profiles of all media exhibit characteristic shapes, which implies that the EDXRS profile is unique to the specific material and significant differences of profiles amongst various liquid substances can be observed. Moreover, the result suggests that non-invasive EDXRS approach would be quite promising in the field of liquid discrimination/recognition.

1. Introduction

Energy dispersive X-ray scattering (EDXRS) is a technique of the energy-dispersive scattering of photons at low angle using a polychromatic incident beam. Under low energy (<100 keV) and low angle (<10°) conditions, coherent scatter is the dominant mechanism for X-ray scatter and is responsible for X-ray diffraction (XRD). Consequently, EDXRS spectrum is a scattering profile from the scattering media and is unique to that specific material. The physics of EDXRS and its potential as a tool for material identification and characterization has been described in detail elsewhere [1–5]. Over the past decade, EDXRS has been widely developed for determining structural characterization of explosive, illegal drugs, and biological systems [6–13]. It has been considered to be a suitable tool for the investigation of liquid systems because of its high speed and good reliability compared with a traditional angular scanning diffractometer [1,2,14–17]. Recently, intermolecular structure of pure liquid and solution has already been investigated extensively at different conditions by means of EDXRS in order to study the local structure of H-bonding, hydration and molecular aggregation [17–22].

Liquid materials such as hazardous liquid fuel, liquid explosives and precursor chemicals are deserved special attention by security screening. Many different approaches have been proposed to address the challenge of liquid identification for security screening, including Raman scattering [23], gas chromatography/mass spectrometry [24], magnetic resonance [25,26], terahertz spectroscopy [27], Hilbert spectroscopy [28] and ion mobility spectrometry [29]. Unfortunately, some of these highly sensitive methods are expensive and required sophisticated instrumentation; furthermore, some approaches require direct contact with the liquid samples generally stored in containers that cannot be opened routinely for inspection. In contrast, EDXRS provides a very good structural insight of disordered systems and may be used to identify and detect

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liquid substances [30,31]. EDXRS is a method to noninvasively inspect unopened liquid containers, its scattering spectra can be collected much faster by using only a few scattering angles, though momentum transfer q ranges obtainable are equal to or larger than those of traditional diffraction [18]. Moreover, most of experimental equipments are cost-low, and the operating procedures of EDXRS are convenient due to its geometric properties allowing the placement of liquid samples stored in sealed cells.

It is well-known that liquids do not exhibit the sharp Bragg peaks presented by crystalline specimen. Instead, they show more or less structureless XRD patterns consisting of weaker, broader features will still be observed, the strength of scattering patterns of which will depend on the degree of molecular order in the material concerned [32]. For example, water will produce weak coherent scattering patterns. So, it has prompted the facetious comment that "XRD patterns of liquid all look alike" [30]. Under the identical probe conditions, the different liquids present a unique scattering profile containing the position, shape, width and intensity of a series of peaks which are governed by the liquid properties. Accordingly, they can be employed as the characteristics for the identification of particular substances. To the best of our knowledge, EDXRS as a tool for liquid material identification has not been reported yet.

In the present work, the X-ray scattering profiles of some liquids were investigated by using EDXRS. The purpose of this work is to describe how liquid materials can be identified by EDXRS in spite of their lack of crystalline structure. More importantly, the experimental tool is intrinsically reliable and potential for use in research into the feasibility of method to identify the presence of liquid precursor chemicals by EDXRS profiles.

2. Experimental section

2.1. Liquid samples

Eleven kinds of liquid samples were measured in this study. The samples were listed as follows: methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, benzene, methylbenzene, *o*-xylene, dichloromethane, trichloromethane and tetrachloromethane. All reagents used in our experiments were analytically pure grade, purchased from Shanghai Chemical Reagents Company, and used without further purification.

2.2. EDXRS experiments

We performed the experiments using the non-commercial energy-scanning diffractometer built in the Institute of Intelligent Machines, Chinese Academy of Sciences, China. The diffractometer consists of (1) a Seifert X-ray generator, (2) a watercooled tungsten X-ray source with 3.0 kW maximum power and a nominal focal spot of 1 × 10 mm, (3) a Silicon Drift Detectors (XR-100SDD), connected to a multichannel analyser (AMPTEK PX4, 1024) channels by an electronic chain for diffraction spectra collection, has an energy detection of 0.14 keV at 5.9 keV (^{55}Fe), (4) a collimator system which focuses the X-ray beam in front of and behind the sample, (5) a step motors for moving the arms supporting the detector, whose minimum step movement leads to a minimum angle incrementum and reproduction of 0.01°, and (6) an adjustable sample holder that was positioned in the optical centre of the diffractometer.

A schematic diagram of the experimental system is shown in Fig. 1. The distance between source and sample is 180 mm, and that of the sample between detectors is 120 mm. The tungsten tube works at 55 kV and 20 mA, thus producing a white spectrum in the low energy range (the bremsstrahlung component of the X-ray source was used). Two vertical slits with 15 mm in height and of variable slit width collimate a parallel beam onto the sample, a horizontal Soller silt and a 0.02 mm in width and 15 mm in height receiving slit, which improve the angular resolution, collimate the scattered beam. The horizontal Soller silt consists of a series of horizontal parallel slits, which is used to define the direction of the scattering beam and produce parallel beam. Such parallel beam is vertical to receiving slit. We can perform the measurements at a fixed scattering angle θ, having a white incident polychromatic beam. A sample of the test liquid sealed in a lucite holder with an internal volume of 2.0 ml, which can avoid evaporation and contamination by moisture in the air, is exposed to X-rays for 5 min. The X-ray intensity of an empty holder is also measured to make corrections for cell scattering. The measuring time was set 5 min so as to obtain 200–8000 counts per experimental sample. This large amount of counts can be achieved, taking account of a significant improvement of signal to noise ratio. All samples were kept at the room temperature.

A scattering parameter q can be expressed by scattering angle θ and X-ray energy E, as shown in the following equation:

$$q = \frac{1}{\lambda}\sin\left(\frac{\theta}{2}\right) = \frac{E}{hc}\sin\left(\frac{\theta}{2}\right) \tag{1}$$

where λ, h, and c are the wavelength of the incident radiation, Planck's constant, and the speed of light, respectively. The unit of E is keV, while that of q is nm^{-1}. It is apparent that the material structure can be interrogated both by holding λ fixed and measuring the scattering as a function of θ. It is generally known that the angular dispersive diffraction technique and the method are used in most standard diffraction measurements, or in an energy-dispersive mode whereby measurements are made at a fixed

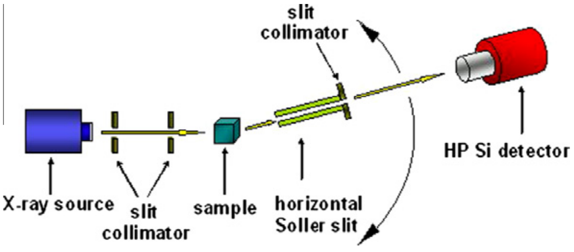

Fig. 1. Sketch of the energy dispersive X-ray scattering spectrometer.