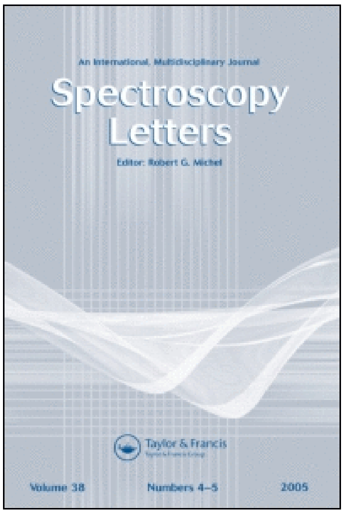

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Comments Concerning the Study of KBr-Contaminated Carbons Using Infrared FT Diffuse Reflectance Spectroscopy

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COMMENTS CONCERNING THE STUDY OF KBr-CONTAMINATED CARBONS USING INFRARED FT DIFFUSE REFLECTANCE SPECTROSCOPY

Key Words: carbons, infrared spectra, diffuse reflection spectroscopy, contamination

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Rochester and associates [1] recently stated: (A) "We here show that the combination of F.t i.r., diffuse reflectance, and a vacuum cell with a heatable stage provides an extremely powerful method for the spectroscopic examination of carbon surfaces *in situ* under a variety of experimental conditions." They showed quite well-structured spectra stated to be those of carbons after treatment with oxygen at temperatures up to 540°C.

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However, they also stated: (B) "A **homogeneous** **mixture** of ca. 6 wt. activated **carbon** **...** **and** **KBr** was evenly spread on the sample stage of a vacuum chamber..." and stated that (C) "Spectra were recorded with reference to background spectra of either KBr alone in the i.r. cell or the **initial** **KBr-carbon** **mixture** in the cell before oxygen treatment." [The bold characters and underlining have been added to the verbatim quotations.] They leave no doubt that they recorded spectra of carbon-KBr **mixtures.**

The purpose of the present comment is not to quibble about the fact that a mere 94 wt. % of KBr has been overlooked, so that statement A is misleading, but to point out, perhaps redundantly, that it is well-known that alkali metal salts enhance the gasification rates and mechanisms of carbonaceous materials [2], potassium salts being of particular value [3]. Although the halides are not very efficient gasification promotors (carbonates are best), their presence does affect gasification rates, e.g., [4].

It is also a fact that a detailed IR spectroscopic study showed that the presence of NaCl markedly altered the pyrolysis of cellulose and the oxidative behavior of the carbons which were formed [5], and that another detailed IR study [6] showed that the presence of potassium (derived from $KHCO_3$) also markedly affected the pyrolysis of cellulose and the oxidative behavior of the carbons which were formed. Further, the two salts produced different effects.

In addition, it is well-known that NaCl and KBr crystals cannot (or, at least, should not) be used as windows for IR cells at temperatures above about 350°C; the windows sublime. In fact, Most alkali halides have appreciable vapor pressures [7]. For KBr, the vapor pressure rises rapidly from 2×10^{-6} torr at 445°C to 1.3×10^{-3} torr at 540°C to 2.5×10^{-2} torr at 627°C [8]. Indeed, vaporization techniques are used for the preparation of salt films having surface areas high enough to be used for IR studies of adsorbed species, e.g., [9-12].

What all this means in view of statements B and C is that the samples Rochester and associates examined consisted of small amounts of carbon contaminated with KBr, and that heating the samples in order to carry out oxidation studies aggravated the situation because the vaporized KBr would have contaminated every previously uncontaminated nook and cranny of the carbon.

The KBr contaminant will affect the reaction(s) of the carbon. Consequently, although IR spectra can be or may be recorded with such samples by the means employed by Rochester and associates, there is no point in doing so, except perhaps with the intention of establishing the effects of the contaminant on the reactivity of the carbon. Of course, to accomplish the latter it will also be necessary to study the reactions of uncontaminated carbon by means of the exact same technique. Whether that can be done remains to be established.

As things stand at present, the technique described by Rochester and associates will, inexorably, lead to wrong results, and should be avoided.

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