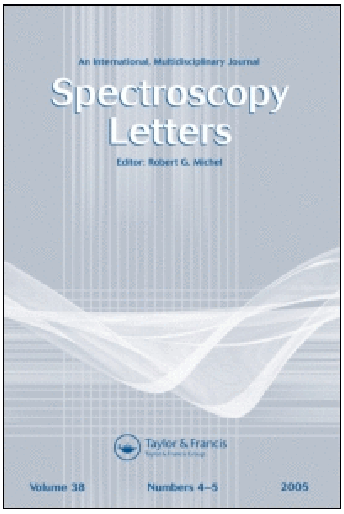

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Use of High-Resolution Mass Spectrometry to Identify Products from Microwave Discharges in COAL-D_2O Mixtures

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USE OF HIGH-RESOLUTION MASS SPECTROMETRY TO IDENTIFY PRODUCTS FROM MICROWAVE DISCHARGES IN COAL-D_2O MIXTURES

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Reactions of carbonaceous materials and H O in microwave discharges are known to produce H_2, HCN, CO, CO_2, and light hydrocarbon gases (primarily C_1 and C_2) in varying amounts. To determine if the solid or the H_2O is the source of hydrogen in formation of the above products, Fu and Blaustein reacted coal and graphite with D_2O.[1] Low-resolution mass spectra of the gaseous products from the D_2O experiments indicated the possibility of non-deuterated and corresponding deuterated compounds in the reaction mixture. Conventional separation and analytical techniques are not applicable to mixtures of this type. This communication describes the use of a high-resolution mass spectrometer, operated at a resolution 35 percent less than theoretically required for separation of the H_2-D doublet, to electrically measure precise masses for mixtures containing micromole amounts of deuterated and non-deuterated light gases.

As the H_2-D doublet is separated by only 0.0015 atomic mass units (amu), a resolution of approximately 20,000 is required for separation of even the C_2 deuterated and non-deuterated hydrocarbons. (Resolution is defined as a 10 percent valley between 2 adjacent mass peaks of equal intensity.) At this resolution the sensitivity of the mass spectrometer is quite low. Precise masses of minor components present in mixtures often cannot be determined using a Nier peak matcher. Although computational methods have been described in the literature to locate peak centers and separate overlapping lines from photoplate data,[2] such techniques are not applicable to the Nier peak matching system used in many laboratories.[3] If accurate mass measurements could be made with more than a 10 percent valley between 2 adjacent masses having different intensities, the instrument resolution could be decreased with a resulting gain in the ion intensity of the mass spectrum of the mixture.

A Consolidated Electrodynamics Corporation model 21-110B high-resolution mass spectrometer was used for this investigation.[4] Precise mass measurements were made using a Nier peak matcher.

To determine if accurate measurements could be made directly at a resolution less than the 20,000 required for the separation of the H_2-D doublet in the C_2 hydrocarbon range, mass measurements were made with the instrument adjusted to produce various degrees of resolution for a known doublet of different ion intensities. The doublet, $C_7H_8^+$-$C_6{}^{12}C^{13}H_7^+$ at m/e 92, present in a toluene-xylene mixture, requires a resolution of 1/20,000 for complete separation as defined above. Results of mass measurements and ion intensities observed with the instrument adjusted to produce valleys of 10 and 75 percent, respectively, are as follows:

		Relative ion intensity		Deviations from theoretical mass (amu)	
Resolution	Valley Pct.	$C_6{}^{12}C^{13}H_7^+$	C_7H_8	$C_6{}^{12}C^{13}H_7^+$	$C_7H_8^+$
1/20,000	10	18	210	0.0000	-0.0002
1/13,000	75	90	1,200	+0.0001	-0.0001

These results demonstrate that a decrease in resolution of 35 percent produces a 5- to 6-fold increase in ion intensity with no loss in accuracy of mass measurement even though the ratio of intensities of the two ions is about 12 to 1.

Table 1 shows the multiplets detected at masses 14-28 in the gases resulting from the reaction of coal and D_2O in a microwave discharge. The presence of CH_4, CDH_3, CD_2H_2, CD_3H, H_2O, HDO, D_2O, C_2H_2, C_2DH, C_2D_2, HCN, CO, and N_2 was established in this mixture. With only two exceptions (CO and N_2) agreement between measured and theoretical masses was better than 1 millimass unit.

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4. Reference to specific makes or models of equipment is made to facilitate understanding and does not imply endorsement of such brands by the Bureau of Mines.

TABLE 1

Microwave Discharge Reaction Products from Coal-D_2O (resolution 1/13,000)

Nominal mass	Measured mass	Actual mass	Δ amu	Empirical formula
14	13.9974	13.9974	0	CO^{++}
	14.0032	14.0031	+0.0001	N
	14.0142	14.0141	+0.0001	CD
	14.0158	14.0156	+0.0002	CH_2
15	15.0221	15.0219	+0.0002	CDH
	15.0236	15.0235	+0.0001	CH_3
16	15.9951	15.9949	+0.0002	O
	16.0298	16.0297	+0.0001	CDH_2
	16.0313	16.0313	0	CH_4
17	17.0028	17.0027	+0.0001	OH
	17.0362	17.0360	+0.0002	CD_2H
	17.0376	17.0376	0	CDH_3
18	18.0091	18.0090	+0.0001	OD
	18.0106	18.0106	0	H_2O
	18.0439	18.0438	+0.0001	CD_2H_2
19	19.0169	19.0168	+0.0001	HDO
	19.0502	19.0501	+0.0001	CD_3H
20	20.0232	20.0231	+0.0001	D_2O
26	26.0026	26.0031	-0.0005	CN
	26.0136	26.0141	-0.0005	C_2D
	26.0154	26.0156	-0.0002	C_2H_2
27	27.0100	27.0109	-0.0009	HCN
	27.0227	27.0219	+0.0008	C_2DH
28	27.9929	27.9949	-0.0020	CO
	28.0041	28.0061	-0.0020	N_2
	28.0273	28.0282	-0.0009	C_2D_2