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The Effect of the Shield Voltage on Appearance Potential Measurements Using a Mass Spectrometer

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In the usual type of mass spectrometer, a small negative voltage is applied to the filament shield as an aid in confining the largest portion of the filament's emission to the region of the electron slit. In measuring the appearance potential (AP) with the mass spectrometer, the obtained values were found to be affected by the shield voltage. To the authors' knowledge, however the effect of the shield voltage on the AP has not yet been discussed, though it is well known that the measured AP is affected by the repeller voltage[1,2] and/or the source magnetic field.[3] In the present note, the cause of the effect of the shield voltage on the AP will be discussed and a procedure to eliminate the effect will be reported.

Experimental

A CEC 21-103C mass spectrometer was used in measuring the AP. The ionization efficiency (IE) curves were treated by the E.D.D. technique[4] after the data had been smoothed by the least-squares method using a computer. The constant, b, used in the E.D.D. calculation was 0.67. Krypton was used as the calibrating gas for the electron energy scale. The ionization potential (IP) of krypton was taken as 14.00 eV. The sample, benzene, and krypton were introduced into the ion source at the same time. The repeller voltage was kept at a constant value[1,2] for all the measurements. The electron trap current was 10 μA; the temperature of the ion source was 250°C.

The IP value of benzene was measured by using two electric circuits, 1) a standard electric circuit, and 2) a modified electric circuit. In the standard circuit of the CEC 21-103C mass spectrometer, the electron accelerating voltage (V_e) and the shield voltage are supplied from the same circuit by changing the value of the resistor, R, in the circuit, as is shown in Fig. 1. Under usual experimental conditions, the shield voltage changes in proportion to V_e, since the value of the resistor between the filament and the shield electrodes is kept constant ($r \simeq 500$ ohm). In the modified circuit, the voltage, V_e, was supplied from a separate circuit and was set with a 10-turn potentiometer (Sakae Tsushin Kōgyō Co., Ltd.), as is shown in Fig. 2, while the shield voltage was set by the same resistor, R, as in the standard circuit. By this circuit, the shield voltage can be set at any value, independent of the V_e.

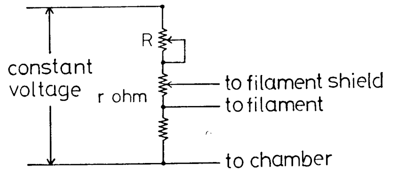

Fig. 1. Diagram of the standard electric circuit for the electron accelerating voltage and the shield voltage of a CEC 21-103C mass spectrometer.

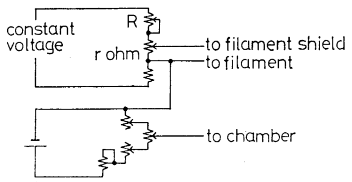

Fig. 2. Diagram of she modified electric circuit for the electron accelerating voltage and the shield voltage.

Results and Discussion

The two IP values of benzene determined in the present study are, in Table 1, compared with those obtained by various other methods.[5-8] As may be seen

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Table I. Ionization potential of benzene obtained by using (a) standard electric circuit, and (b) modified electric circuit

	eV
Photoelectron Spectroscopy[5]	9.24
Spectroscopy[6]	9.24_8
Photoionization[7]	9.24_1
Electron Impact (RPD)[8]	9.21
This work[a]	9.52 ± 0.1
This work[b]	9.20 ± 0.1

in the table, the IP value obtained by using the modified circuit agrees reasonably well with the literature values, while that obtained by using the standard circuit is considerably higher. A little higher AP values were obtained for various ions from disubstituted benzenes,[9] too, when the standard circuit was used.

Table 2. Ionization potentials of krypton measured under various shield voltages

Shield voltage (mV)	Ionization potential (eV) (uncorrected)
$1.0\times r$	13.40 ± 0.1
$1.5\times r$	13.30 ± 0.1
$2.0\times r$	13.05 ± 0.1

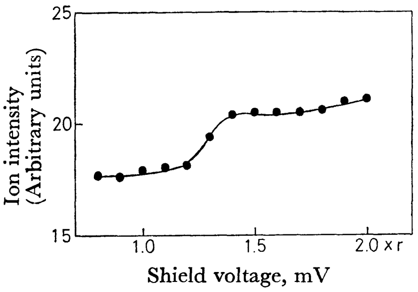

Fig. 3. Variation of the ion intensity of krypton (m/e 84) with the shield voltage at the electron accelerating voltage of 15.0 eV (uncorrected), and at ion accelerating voltage of about 1000 V.

To clarify the cause of these results, the IP of krypton was measured at three shield voltages corresponding to current flows of 1.0, 1.5, and 2.0 mA through the resistor ($r\simeq500$ ohm). The values thus obtained are shown in Table 2. The variation in the krypton-ion (m/e 84) intensities with the shield voltage obtained at the electron accelerating voltage of 15.0 eV is shown in Fig. 3. From Figure 3 and Table 2, it may be seen that the ion intensity at a constant electron accelerating voltage increases with an increase in the shield voltage, and that the observed IP for krypton decreases with an increase in the shield voltage. Hence, if the IE curves of the two compounds are measured at different shield voltages, the difference between the two apparent IP's observed will be different from the difference between the true IP's for the two compounds, since different shield voltages exert different influences on the ion intensities of the two compounds. When the IP of benzene is measured by using the standard electric circuit of the CEC 21–103C mass spectrometer and when krypton is used as the calibrating gas for the electron energy scale, different shield voltage are used in each case—*i.e.*, for benzene, about $0.9\times r$ (mV), and for krypton, about $1.4\times r$ (mV). If the factors of the effects due to the shield voltage on the observed IP's of benzene and krypton are taken as $A(C_6H_6)$ and $A(Kr)$ respectively, in this case the following relation can be expected by referring to Table 2, since the shield voltage in the case of benzene is lower than that in the case of krypton:

$$A(C_6H_6) < A(Kr) \tag{1}$$

If the instrumental factors due to the contact potential, *etc.*, are taken as X, then the apparent IP's of benzene, $IP(C_6H_6)$, and of krypton, $IP(Kr)$, are given by the following equations respectively:

$$IP(C_6H_6) = \text{true}\,IP(C_6H_6) + X - A(C_6H_6) \tag{2}$$

$$IP(Kr) = \text{true}\,IP(Kr) + X - A(Kr) \tag{3}$$

Since benzene and krypton are introduced into the ion source simultaneously, X is the same for both equations. By subtracting Eq. (2) from Eq. (3), we obtain:

$$IP(Kr) - IP(C_6H_6) = \text{true}\,IP(Kr) - \text{true}\,IP(C_6H_6) - A(Kr) + A(C_6H_6) \tag{4}$$

From Eq. (4), it may be seen that the difference between the apparent IP's is smaller than that between the true IP's, because $A(C_6H_6) < A(Kr)$ in this case. Accordingly, to calibrate the electron energy scale, let the apparent IP of krypton, IP(Kr), be equal to 14.00 eV; then the IP value of benzene obtained will be somewhat higher than the true IP value. This may be the reason why a high IP value, as is shown in Table 1, was obtained when the IP was estimated without taking the effect of the shield voltage into account. On the other hand, the IP value obtained at a constant shield voltage for both benzene and krypton is in good agreement with those of the other workers. At least a part of the reason why a little higher AP values than those accepted were obtained previously[9] for some disubstituted benzenes may be understood in terms of the same explanation. The effect of the shield voltage on the AP may be due mainly to the fact that the electrons from the filament are somewhat accelerated by the shield voltage.

When a CEC 21-103C mass spectrometer is used to measure the AP, a compound which has almost the same ionization potential as that of the sample should be used as the calibration compound for the electron energy scale; otherwise, the shield voltage should be kept at a constant value for measuring the IE curves for both the sample and the calibration compound.

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