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Negative Ions Formed by Vacuum Spark Discharge. II.[1] Relative Sensitivity Coefficients for Negative Ions of the Elements Contained in Compressed Aluminium Powder Electrodes for Spark Source Mass Spectroscopy

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The relative sensitivity coefficients for negative ions of 15 elements contained in compressed aluminium powder electrodes were measured by spark source mass spectroscopy. The relative sensitivity coefficients for the halogens and group VIB elements were found to be the largest, the difference of relative sensitivity coefficients between the elements being larger than in the case of positive ion relative sensitivity coefficients. The logarithm of the relative sensitivity coefficients of negative ions are linearly correlated to the electron affinities of the elements.

A study on negative ion spark source mass spectroscopy has been carried out with a Mattauch-Herzog type double focusing mass spectrograph. The formation of atomic negative ions of 48 elements was reported.[1] Formation of negative ions with a spark discharge type ion source is more difficult than that of positive ions. No negative ion formation took place in rare gas elements, alkaline earth elements, Zn, Cd, Hg, Mn, Re, and rare earth elements. On the other hand, negative ion formation is easy for halogen elements and the group VIB elements. Qualitative investigation was made on the relation between the formation of atomic negative ions by spark discharge and the polarity of the electron affinities of the elements.[1] In the present study, the relative intensities of the negative ions formed by the spark discharge ion source were measured and the results compared with the reported electron affinities of the elements.

The relative sensitivity coefficients of positive ions in spark source mass spectroscopy reported by various authors[2–5] are correlated to the square root of the ionization potentials of the elements and to the heats of sublimation and dissociation energies of the compounds contained in the electrodes. Various empirical formulas[6,7] have been applied to the chemical analysis of solids.[8–10] However, except for the work of Schuy *et al.*,[11] Hintenberger *et al.*,[12] Kishi *et al.*,[13] and Kodera *et al.*,[14] few mass spectroscopic studies have been made on negative ions formed by a spark discharge ion source. The relative sensitivity coefficients of negative ions seem to have hardly been examined at all. This might be due to the difficult formation of negative ions by spark discharge as compared with positive ions.[15]

The results of this study can be applied to the chemical analysis of solids. The relative sensitivity coefficients for negative ions are necessary for applying spark source nagative ion mass spectroscopy to chemical analysis. The present study deals with the relative sensitivity coefficients of negative ions formed by the spark discharge of the elements contained in compressed aluminium powder electrodes, the results being correlated to the electron affinities of the elements.

Experimental

Apparatus. A Mattauch-Herzog type double focusing mass spectrograph equipped with an r. f. spark discharge ion source was used. Details of the instrument were reported.[16–18] Operational conditions: spark voltage 20 kV; pulse width, 200 μs; repetition rate 100 s^{-1}; ion accelerating potential, 15 kV for both positive and negative ions.

Materials. Powdered samples containing an equal weight (1.28% for each element) of 49 common elements (SPEX MIX 1000; SPEX MIX INDUSTRIES INC.), and powdered samples containing 10 noble metal elements (SPEX MIX 1041) were used. Various metal alloy samples were also used (Table 6). Compounds and gravity factors for SPEX MIX 1000 are given in Table 1. SPEX MIX 1041 contains 9.32% Au, Ga, Hf, In, Ir, Pd, Pt, Re, Rh, and Ru by weight, some of them being solutions and the others salts or powdered metals. The powdered samples were ground down to 325 mesh with a ball-mill for a few hours. In order to compress them, the samples were mixed thoroughly with pure aluminium powder in 1:1 ratio by weight (Mitsuwa-Kagaku Co. Ltd., purity 99.999%; impurities Cu, As, B (each 1 ppm), Mg, Si (each 0.5 ppm)). In negative ion spark source mass spectra, background peaks of hydrocarbon ions are usually very intense. Thus graphite powder is not suitable as compressing material, since C_n^-, C_nH^-, and $C_nH_2^-$ ion peaks are very intense in the spark discharge of a graphite electrode, the peaks interfering with the mass spectral peaks of the sample elements. The powders were compressed[19] into pellets, 12 mm × 3 mm × 1 mm with an 8 t/cm^2 press. Aluminium powder only was also compressed in order to measure background peak spectra.

Procedure for Calculating RSC. Positive ion mass spectra and negative ion mass spectra were both recorded on an Ilford Q2, 30 × 150 mm^2 photographic plate. Characteristic curves of the emulsions were constructed from positive ion spectra using the isotope peaks of Pt^+ and Zn^+ ions from the spectra obtained by the spark discharges of different exposure times. In a characteristic curve, the abscissa represents the logarithm of (monitor ion current) × (isotopic abundance ratio), and the ordinate the values $D=\log(I_0/I)$ or $\Delta=\log((I_0-I)/I)$. In order to estimate weak line intensity, Δ (Seidel function[20]) in which the curve is linear in the region of low ion intensity, was used. A characteristic curve obtained by means of positive ion mass spectra was used to calculate negative ion peak intensity. It was assumed that the response of the photographic emulsion is the same for positive and negative ions.

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TABLE 1. COMPOUNDS AND GRAVITY FACTORS FOR SPEX MIX 1000

Element	Compound	Grav. factor	Element	Compound	Grav. factor
Aluminium	Al_2O_3	1.89	Manganese	$MnCO_3$	2.09
Antimony	Sb_2O	1.26	Mercury	HgO	1.08
Arsenic	As_2O_3	1.32	Molybdenum	MoO_3	1.50
Barium	$BaCO_3$	1.44	Nickel	NiO	1.27
Beryllium	BeO	2.77	Niobium	Nb_2O_5	1.43
Bismuth	Bi_2O_3	1.11	Phosphorus	$(NH_4)_2HPO_4$	4.26
Boron	H_3BO_3	5.72	Potassium	K_2CO_3	1.77
Bromine	NH_4Br	1.23	Rubidium	$RbCl$	1.41
Cadmium	CdO	1.14	Selenium	SeO_2	1.41
Calcium	CaF_2	1.95	Silicon	Si	1.00
Cerium	CeO_2	1.23	Silver	Ag_2O	1.07
Cesium	$CsNO_3$	1.47	Sodium	Na_2CO_3	2.30
Chlorine	NH_4Cl	1.51	Strontium	$SrCO_3$	1.68
Chromium	Cr_2O_3	1.46	Tantalum	Ta_2O_5	1.22
Cobalt	CoO_2	1.41	Tellurium	TeO_2	1.25
Copper	CuO	1.25	Thallium	Tl_2O_3	1.12
Fluorine	CaF_2	2.05	Thorium	ThO_2	1.14
Gallium	Ga_2O_3	1.34	Tin	SnO_2	1.27
Germanium	GeO_2	1.44	Titanium	TiO_2	1.67
Iodine	NH_4I	1.14	Tungsten	WO_3	1.26
Indium	In_2O_3	1.21	Uranium	UO_2	1.18
Iron	Fe_2O_3	1.43	Vanadium	V_2O_5	1.79
Lead	PbO	1.08	Zinc	ZnO	1.24
Lithium	Li_2CO_3	5.32	Zirconium	ZrO_2	1.35
Magnesium	MgO	1.66			

In order to compare the results with those reported and to confirm the method, the relative sensitivity coefficients of positive ions were first measured and then those of negative ions. The procedure for calculation is essentially the same for positive and negative ion mass spectra. In the latter, however, the background hydrocarbon peaks are very intense and seem to originate from the diffusion pump oil. For the purpose of reducing the background peak intensity, the cryopumping system[21] was considered, but the discharge between the cryopumping plate (earth potential) and the ion accelerating plate (−15 kV from earth) prevented this attempt. It was thus necessary to make background subtraction in the spectra. In the negative ion spark spectra, the mass spectral peaks were broadened by discharge between the accelerating electrode and the earth (defining) electrode. Line width correction was also necessary.

The procedure for calculating the relative sensitivity coefficients is as follows. (1) The relative ion intensities of the isotope peaks are obtained from the characteristic curve, and correction for isotopic abundance ratio is made. (2) The data are further corrected for peak width at half maximum, and the emulsion sensitivity is corrected by means of the $(m)^{-1/2}$ law.[22] (3) Background subtraction is made. For the positive ion mass spectra, multicharged peak intensity is subtracted by estimation from the non-integral isotopic ion intensities. Background peak intensities, *e.g.*, hydrocarbon ions and Al_n^+ ions, are subtracted from the Al/Al blank spark spectra by means of the monitor ion current.

In the negative ion mass spectra, no multicharged negative ion peaks were detected,[1] but background hydrocarbon peaks were very intense. Because of the electron current, the monitor ion current was unreliable and could not be used to estimate the background ion peak intensity. In the negative ion spectra, the m/z 34 peak was not a sample ion peak but a background ion peak. The background peak intensities of the mass spectra of the Al/Al spark spectra were normalized (m/z 34 peak intensity$=1$), and subtracted from those of the sample/sample spark spectra, in which peak intensities were also normalized (m/z 34 peak intensity$=1$). When the background peak intensity exceeded 50% of the sample peak intensity, no peak intensity was estimated. In A/B spark spectra, A and B indicate the substances in the vacuum spark discharge electrodes.

Results and Discussion

Positive Ion Relative Sensitivity Coefficients. The relative sensitivity coefficients of positive ions for 49 common elements are given in Table 2, and those of 10 noble metal elements in Table 3.

The relative sensitivity values are larger than those reported,[6] except for those for the elements Fe, Co, Si, V, and Cu. The difference between the two values for alkali metal elements is very large. For the halogen elements, the relative sensitivity values are larger than the reported values, the discrepancy between the two values being larger than that for the other elements. The alkali metal elements and halogen elements are present as carbonate and ammonium salt, respectively, and are probably more easily volatilized than other compounds in the spark discharge. The discrepancy in the relative sensitivity coefficients can thus be explained by the assumption that the spark discharge condition in this experiment is more discriminative for volatilization of the compounds contained in the spark electrodes. Aluminium

TABLE 2. RELATIVE SENSITIVITY COEFFICIENTS FOR POSITIVE IONS OF 49 COMMON ELEMENTS (Li, Be, B, Al, AND Hg NOT INCLUDED)

Element	RSC[a]	Run	σ[b]	Ref. 6[c]	Element	RSC[a]	Run	σ[b]	Ref. 6[c]
Na	22.1	2	0.70	3.5	Cl	2.1	3	1.1	0.45
Rb	17.6	4	5.3	3.4	Ag	2.0	4	0.44	1.3
Cs	17.3	4	5.2	5.0	Ce	1.9	4	0.67	1.1
K	13.6	4	5.0	3.8	Sn	1.6	4	0.29	1.2
Tl	7.5	4	2.4	2.4	U	1.4	2	0.41	0.73
Ba	4.8	4	3.3	1.7	Mn	1.4	4	0.066	1.2
Bi	4.1	3	0.92	1.2	As	1.2	4	0.22	0.99
Pb	3.9	3	0.69	1.6	P	1.2	4	0.47	0.83
I	3.7	4	0.94	0.78	Cr	1.1	4	0.43	1.0
Te	3.6	4	0.90	0.75	Ge	1.1	4	0.18	0.85
Br	3.2	4	1.3	0.45	Ti	1.1	4	0.32	0.85
In	3.2	4	0.79	1.8	Fe	1.0	4	—	1.0
Zn	2.9	4	0.68	0.98	Co	0.86	4	0.11	1.0
Ta	2.8	2	1.9	0.56	Zr	0.84	3	0.24	0.51
Mg	2.7	4	0.61	2.0	Nb	0.80	4	0.30	0.65
Sr	2.6	4	0.56	1.5	Si	0.79	1	—	0.98
Se	2.5	4	0.73	0.64	V	0.79	4	0.24	0.80
Ga	2.5	4	0.43	1.8	Cu	0.77	3	0.19	0.79
Cd	2.3	4	0.81	0.81	Ni	0.73	4	0.22	0.63
Sb	2.2	4	0.40	0.89	F	0.69	4	0.22	0.18
Ca	2.2	3	0.40	1.8	W	0.67	1	—	0.55
Th	2.1	1	—	0.53	Mo	0.66	4	0.33	0.75

a) Mean of each run. b) Standard deviation of each value. c) SPEX MIX 1000, compressing material graphite.

TABLE 3. RELATIVE SENSITIVITY COEFFICIENTS FOR POSITIVE IONS OF 10 NOBLE METAL ELEMENTS

Element	RSC[a]	Run	σ[b]	Element	RSC[a]	Run	σ[b]
In	1.41	4	0.18	Rh	0.335	4	0.048
Ga	1.00	4	—	Pt	0.320	4	0.10
Hf	0.577	4	0.11	Pd	0.320	4	0.057
Au	0.361	4	0.11	Ru	0.305	4	0.043
Re	0.352	4	0.064	Ir	0.305	4	0.083

a) Mean of each run. b) Standard deviation of each value.

powder was used as compressing material, and the spark voltage was 20 kV; Konishi used graphite, the spark voltage being 40 kV.[6]

The standard deviation σ is large for the elements Ba, Ta, and Cl, but less than 40% for the other elements (Table 2). This value is usually given[23] on spark source mass spectroscopy.

Indium and Ga have the largest relative sensitivity values, and Ru and Ir the smallest values (Table 3). The standard deviation of each relative sensitivity value is less than 30%. This might be due to the fact that the relative sensitivity values do not differ a great deal between these elements as in the case of 49 common elements (SPEX MIX 1000). Nearly the same parts and the linear portion of the emulsion characteristic curve could be used for estimating the peak intensity.

Both SPEX MIX 1000 and SPEX MIX 1041 contain Ga. The relative sensitivity values of the noble metal elements can be normalized to Fe=1 by multiplying all values by 2.47. These relative sensitivity values of 54 elements are plotted against the $(\text{I.P.})^2$ in Fig. 1. We see that the relative sensitivity coefficients are inversely correlated with the $(\text{I.P.})^2$, by a gradient of *ca.* −1.0. The result is in line with other results reported.[6,7] Na, Te, Zn, and the halogen elements deviate upward, and the transition metal elements and the noble metal elements deviate downward from the straight line. This might be due to the fact that the heats of evaporation of the transition metal elements are large as compared with those of the other typical elements.[6]

Negative Ion Relative Sensitivity Coefficients. The relative sensitivity coefficient values for negative ions were obtained for 15 of the 49 common elements, and for 8 of the 10 noble metal elements. No relative sensitivity coefficients were obtained for the other elements, since no negative ion peaks for these elements were detected or the peak intensities were too low to estimate the relative sensitivity coefficients. The results are given in Table 4 for the 15 common elements, and in Table 5 for the 8 noble metal elements, with the published values of electron affinities.[24–34] N and σ indicate run number and standard deviation as in Tables 2 and 3.

In Table 4, a large standard deviation is observed

Table 4. Relative sensitivity coefficients for negative ions of 15 common elements

Element	RSC[a)]	Run	σ[b)]	E.A./eV	Element	RSC[a)]	Run	σ[b)]	E.A./eV
Cl	1.5	2	0.16	3.628	As	4.9×10^{-3}	4	3.7×10^{-3}	1.1
I	<u>1.00</u>	4	—	3.076	Ni	4.6×10^{-3}	3	1.8×10^{-3}	1.28
Br	9.2×10^{-1}	3	4.4×10^{-2}	3.363	P	4.2×10^{-3}	3	4.4×10^{-4}	0.78
Te	2.0×10^{-1}	4	6.7×10^{-2}	1.96	Ge	3.6×10^{-3}	3	3.0×10^{-3}	1.4
Se	1.3×10^{-1}	4	3.4×10^{-2}	2.1	Si	2.8×10^{-3}	4	2.0×10^{-3}	1.39
Ag	2.0×10^{-2}	3	1.0×10^{-2}	1.303	Cr	1.2×10^{-3}	2	7.2×10^{-4}	0.98
Sb	9.8×10^{-3}	3	5.0×10^{-3}	0.94	Na	9.0×10^{-4}	4	2.5×10^{-4}	0.41
Cu	5.3×10^{-3}	2	1.3×10^{-3}	1.226					

a) Mean of each run. b) Standard deviation of each value.

Table 5. Relative sensitivity coeffients for negative ions of 8 noble metal elements

Element	RSC[a)]	Run	σ[b)]	E.A./eV	Element	RSC[a)]	Run	σ[b)]	E.A./eV
Au	<u>1.00</u>	2	—	2.128	Ru	1.4×10^{-1}	2	1.6×10^{-2}	1.49
Pt	3.0×10^{-1}	4	6.4×10^{-2}	2.3086	Rh	1.4×10^{-1}	2	5.0×10^{-3}	1.68
Ga	2.9×10^{-1}	2	6.4×10^{-2}	0.3	Ir	1.4×10^{-1}	2	3.0×10^{-2}	1.97
Pd	1.6×10^{-1}	4	2.8×10^{-2}	1.03	In	7.0×10^{-2}	2	3.5×10^{-3}	0.2

a) Mean of each run. b) Standard deviation of each value.

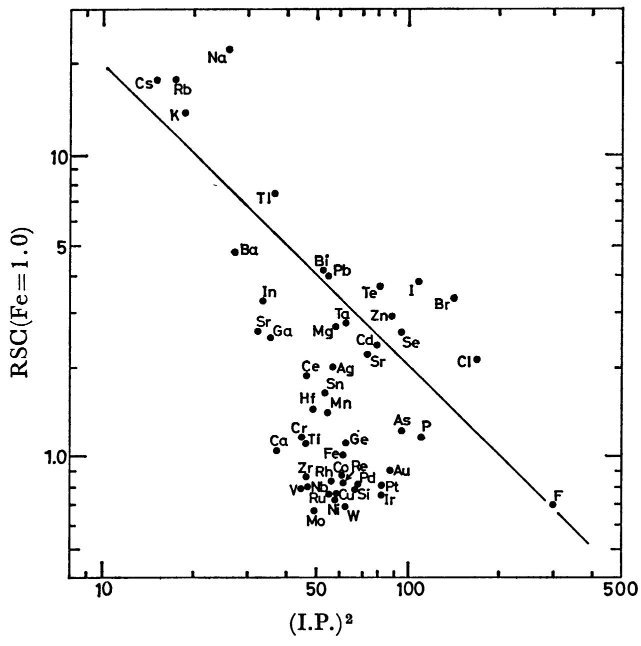

Fig. 1. Relation between the relative sensitivity coefficients for positive ions *versus* (I.P.)^2.

for the elements of low relative sensitivity coefficient values except Cu and Na. For the elements of high relative sensitivity coefficient values, such as Cl, I, and Br, the standard deviation is small. There are two possible reasons: (1) In the calculation of the relative sensitivity coefficients of negative ions, a background subtraction procedure is involved, the background peak intensity becoming relatively larger for a negative ion peak of weak intensity than for one of strong intensity. (2) The absolute values of the relative sensitivity coefficients for negative ions are diverse covering the range 1—10^{-3}. It is necessary to use the non-linear portion of the emulsion characteristic curve for estimating the peak intensity.

On the other hand, for the noble metal elements (Table 5), the standard deviation for each relative sensitivity coefficient value is smaller than 20%. This might be due to the fact that the relative sensitivity coefficient values for the negative ions of these elements do not diverge so widely as in the common elements. The values cover the range only 1—10^{-1}. Thus the linear portion of the emulsion characteristic curve can be used for estimating the peak intensity. Of noble metal elements, no Hf^- and Re^- ions were detected. Au^- and Pt^- were the most intense, and Ir^- and In^- were the least intense.

It is desirable to estimate the relative sensitivity coefficients of negative ions with use of samples which contain elements with near values of the relative sensitivity coefficients. Various metal alloy samples were also examined (Table 6). In these samples, the concentration of each element was not certain. The positive ion intensity ratio of the elements was measured first, the ratio being considered to be the concentration ratio of the elements in samples. The negative ion intensity ratio was then estimated, and the ratio was divided by the positive ion intensity ratio. This quotient was considered to be the relative sensitivity coefficient for the negative ions of these elements. The results are given with the published values of the electron affinity of the elements (Table 6). The run number is 1 for all the elements, no standard deviation being given.

From the results of the experiment with the Pt–Au–Ag–Pd–Cu–Zn alloy we see that the relative sensitivity coefficients of the elements Pt and Au are 1:0.4 (0.3:1 in the results from SPEX MIX 1041). The discrepancy might be due to the difference in the state of the compounds contained in samples. For the other elements, the values of the relative sensitivity coefficients are in the same order between the two samples, though the absolute values hardly change. For example, Ni^-:Cu^- is 1:1.3 for Ni–Cu alloy, and 1:1.2 for the SPEX MIX 1000. Ni^-:Cr^- is 1:0.20 for the Ni–Cr alloy, and 1:0.26 for the SPEX MIX

Table 6. Relative sensitivity coefficients for negative ions of the elements contained in various metal alloys

Element	Positive ion intensity ratio	Negative ion intensity ratio	RSC	E.A./eV
(1) Nichrom-1				
Fe	1.0	1.0	1.0	0.58
Ni	1.13	10.1	9.7	1.28
(2) Nichrom-2				
Ni	1.0	1.0	1.0	1.28
Cr	0.42	0.087	0.20	0.98
(3) Meteorite				
Fe	1.0	1.0	1.0	0.58
Ni	0.081	0.76	9.5	1.28
(4) Ni-Cu Alloy				
Ni	1.0	1.0	1.0	1.28
Cu	0.12	0.17	1.3	1.226
(5) Ni-Co Alloy				
Ni	1.0	1.0	1.0	1.28
Co	0.091	0.080	0.88	0.94
(6) Pt-Rh Alloy				
Pt	1.0	1.0	1.0	2.3086
Rh	1.17	0.28	0.24	1.68
(7) Pt-Au-Ag-Pd-Cu-Zn Alloy				
Pt	1.0	1.0	1.0	2.3086
Au	1.00	0.41	0.4	2.128
Ag	54.4	2.5	0.050	1.303
Pd	34.0	1.3	0.040	1.03
Cu	25.8	2.3	0.10	1.226
Zn	4.4	—	—	−0.67

1000. Pt^-: Rh^- is 1:0.24 for the Pt–Rh alloy, and 1:0.48 for the SPEX MIX 1041.

We see that the relative sensitivity coefficient values for the elements of large electron affinity values are large, and small for the elements of small electron affinity values (Tables 4, 5, and 6). The logarithm of the relative sensitivity coefficients of negative ions versus the published values of the electron affinities of the elements are plotted. The results are given for the samples of SPEX MIX 1000 and SPEX MIX 1041, respectively (Figs. 2 and 3). The logarithms of the relative sensitivity coefficients has a rough linear correlation to the electron affinities of the elements. Se and Te deviate upward from the linear line, but the reported values of the electron affinities of Se and Te diverge from 2.2 eV[23] to 3.7 eV,[35] and from 2.1 eV[36,37] to 3.6 eV,[35] respectively (Fig. 2). Correlation seems to exist between the logarithm of the relative sensitivity coefficient and the electron affinity of the element. Ga having low melting point shows upward deviation.

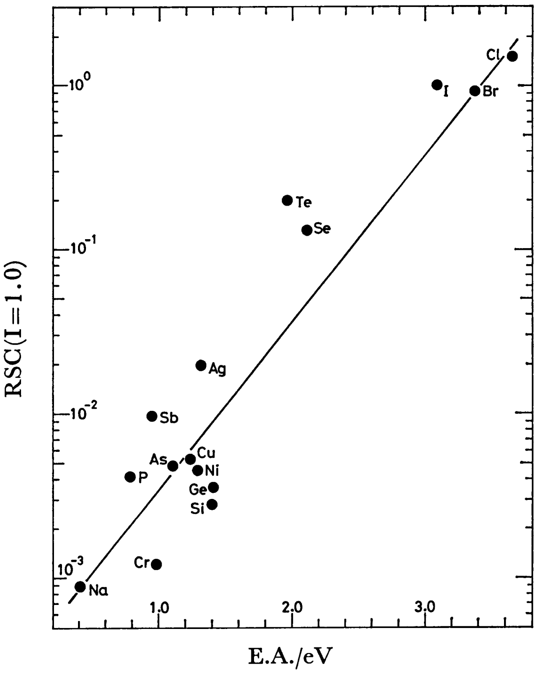

Fig. 2. Relation between the logarithm of the relative sensitivity coefficients for negative ions of 15 common elements *versus* the electron affinities of the elements.

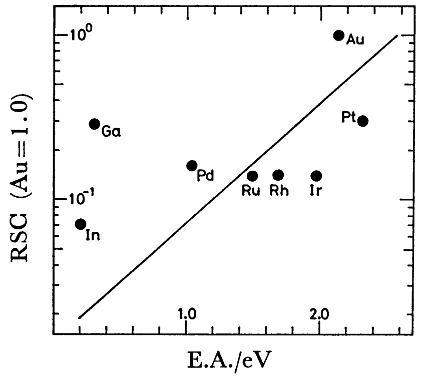

Fig. 3. Relation between the logarithm of the relative sensitivity coefficients for negative ions of 8 noble metal elements *versus* the electron affinities of the elements.

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