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Tutorial IBT-001

Introduction of Materials into  
Ion Sources

Use of Volatile Chemical Compounds

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The use of metal ions is required for a wide range of applications. Metal ions are often difficult to introduce into ion sources and known techniques such as evaporation furnaces or sputtering techniques do not always lead to the desired success. Therefore, the MIVOC<sup>1</sup> method for generating metal ions has proven to be favorable for a large number of metals and was first proposed by [Ärje et al. 1993]. This method uses metallo-organic compounds whose vapor pressures at room temperature allow the compound to be introduced as a gas into the ion source via a precision inlet valve.

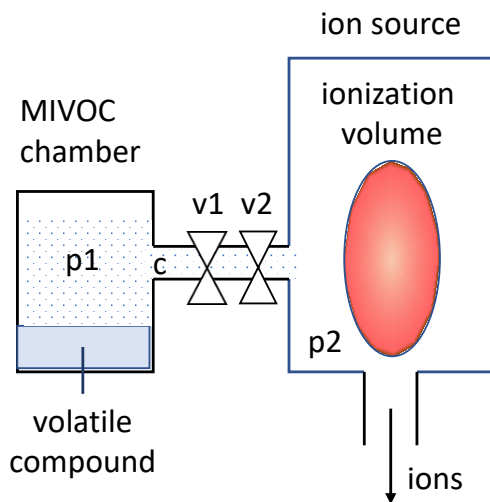


Figure 1: Principle diagram for the MIVOC method for loading the ionization volume of ion sources.  $p_1$  – saturated vapour pressure of the used chemical compound,  $p_2$  – pressure inside the ion source,  $c$  – conductance of the transmission line,  $v_1$  – valve for a pump connection,  $v_2$  – lock valve.

The generalized principle scheme for the use of the MIVOC method is shown in Figure 1 for a typical application with an ECRIS. The substance used is placed in a MIVOC chamber and a saturated vapor pressure is formed at a certain vacuum with the pressure  $p_1$ . To ensure clean conditions when introducing the gas into the ion source, the chamber area and the gas transport section are first pumped down to the pressure  $p_1$ . Connection to a backing pump is made via valve  $v_1$  with valve  $v_2$  closed. After the appropriate working pressure has been reached, the pumping process is terminated by closing the valve  $v_1$  in the direction of the pump, and valve  $v_2$  is opened. The gas can then flow into the ion source at pressure  $p_2$ . The design of the gas transport section with a conductance  $c$  based on this must also be taken into account here.

Since even small amounts of gas are sufficient for source loading, it is possible to operate with compounds of metals, solids or liquids that have a vapour pressure of the order  $10^{-3}$  mbar (for example for ECRIS) or lower of up to about  $10^{-5}$  mbar for EBIS. The limit for the lowest usable vapour pressure here is the conductance of the gas injection system.

<sup>1</sup>MIVOC: Metal Ions from Volatile Compounds

The technical realization of the MIVOC method can generally be done in two ways:

1. If the vapor pressure at room temperature is about 10 mbar or more, a mass flow controller with a piezoelectric valve can be used.
2. Vapor pressures of about 0.01 mbar are realized via the temperature control of the MIVOC chamber and the material inlet into the ion source.

To avoid condensation in the gas transfer line, it is necessary to control the temperature profile in the pipeline. A temperature higher than that of the MIVOC chamber is maintained in the gas transfer system. This can be achieved by means of corresponding, possibly regulated heating coils in the gas transfer system.

Values for vapour pressures of various compounds are often not available in the literature. This makes it necessary to calculate vapor pressures from available data sets. If the temperature of the melting point or the entropy of vaporization at the melting point are known, the vapour pressure at room temperature can be estimated [Koivisto et al. 1994, Ullrich 1997, Ullrich et al. 1998].

Starting from the Clausius-Clapeyron equation which is approximately valid for vapor pressure curves

$$\frac{d \ln P_{V_p}}{dT} = \frac{\Delta S_V}{\Delta Z RT^2} \quad (1)$$

with  $P_{V_p}$  – vapor pressure,  $T$  – temperature,  $\Delta S_V$  - enthalpy of vaporization,  $\Delta Z$  – compressibility and  $R$  – molar gas constant the following simplified relationship is obtained [Weast 1978]

$$\ln P_{V_p} [\text{mbar}] \approx 0.75 \frac{\Delta S_v [\text{kJ/mol}] \Delta T [\text{K}]}{0.15 \Delta T [\text{K}] - T [\text{K}]} + 2.881 \quad (2)$$

$\Delta S_v$  is the entropy of vaporization<sup>2</sup> and is generally available in tabular form. Further applies

$$\Delta T = T - T_b$$

with  $T_b$  – boiling point of the compound.

For a more precise estimation, a modified Watson method [Lyman et al. 1990] can be used, which can be derived from the Clausius-Clapeyron equation (1) and whose range of application includes pressures between  $10^{-3}$  mbar to about  $10^{-7}$  mbar. The method described here only requires knowledge of the melting temperature  $T_b$  as substance-specific parameter. A more detailed description of the modified Watson method is given by [Ullrich 1997] which is followed here.

<sup>2</sup>The vaporization entropy  $\Delta S_v$  describes the change in entropy of a liquid during the transition to the gas phase.

The temperature dependence of the evaporation enthalpy can be determined via

$$\Delta S_V = \Delta S_{V_b} \left( \frac{1 - T/T_c}{1 - T_b/T_c} \right)^m \quad (3)$$

with  $\Delta S_{V_b}$  – enthalpy of vaporization at the melting point,  $T_c$  – critical temperature<sup>3</sup> and  $m$  – substance-specific parameter.

Here for liquids applies  $m = 0.19$  and for solids yields

$$m = \begin{cases} 0.36 & \text{for } T_{Q_b} > 0.6 \\ 0.80 & \text{for } 0.6 > T_{Q_b} > 0.5 \\ 1.19 & \text{for } T_{Q_b} < 0.5 \end{cases}$$

with  $T_{Q_b} = T/T_b$ . Assuming

$$T_c \approx \frac{3}{2} T_b$$

Equation (3) can be transformed to

$$\Delta S_V \approx \Delta S_{V_b} (3 - 2T_{Q_b})^m \quad (4)$$

Inserting Equation (4) in equation (1) gives

$$\ln P_{V_p} \approx - \frac{\Delta S_{V_b}}{\Delta Z_b R T_b} \left[ \left( \frac{(3 - 2T_{Q_b})^m}{T_{Q_b}} + 2m (3 - 2T_{Q_b})^{m-1} \ln T_{Q_b} \right) \Bigg|_1^{T_{Q_b}} - 4m(m-1) \underbrace{\int_1^{T_{Q_b}} (3 - 2T_{Q_b})^{m-2} \ln T_{Q_b} dT_{Q_b}}_{\approx 0} \right]$$

and thus final

$$\ln P_{V_p} \approx \frac{\Delta S_{V_b}}{\Delta Z_b R T_b} \left[ 1 - \frac{(3 - 2T_{Q_b})^m}{T_{Q_b}} + 2m(3 - 2T_{Q_b})^{m-1} \ln T_{Q_b} \right] \quad (5)$$

<sup>3</sup>The critical temperature is the temperature of substances at which the liquid-gas phase transition proceeds without any change in volume. As the temperature belonging to the critical point, it defines the end point of the vapor pressure curve in the phase diagram and is thus the temperature above which liquefaction of a gas is no longer possible, no matter how high the pressure.

According to [Lyman et al. 1990] the entropy at the melting point can be described via

$$\frac{\Delta S_{V_b}}{T_b} = K_S (8.75 + R \ln T_b) \quad (6)$$

with  $R = 1.987 \text{ cal}/(\text{mol}\cdot\text{K})$  and  $T_b$  in Kelvin.  $K_S$  is a tabulated structure coefficient.

If equation (6) is substituted into equation (5), the vapor pressure can be calculated in atmospheres or in multiples of 760 Torr. The compressibility can be approximated to  $\Delta Z_b = 0.97$  in this estimation [Lyman et al. 1990]. [Ullrich 1997] indicates that the error of the calculations is below 50% in the pressure range between  $10^{-3}$  mbar up to  $10^{-7}$  mbar.

It should be noted that the saturation evaporation pressure is constant at constant temperature. The time it takes for the saturation evaporation pressure to build up in a closed volume can be calculated according to [Koivisto et al. 1994]

$$t_{sat} [\text{s}] = \frac{p_{sat} [\text{mbar}] V_{MIVOC} [\text{l}]}{N_{max} \left[ \frac{\text{mbar l}}{\text{s mg}} \right] m [\text{mg}]} \quad (7)$$

with  $p_{sat}$  – saturation pressure,  $V_{MIVOC}$  – volume of the MIVOC chamber,  $N_{max}$  – maximum evaporation rate of the compound and  $m$  – mass of the used compound. With commonly used MIVOC chambers, the saturation time is a maximum of a few 10 ms. It is also important to know that with common MIVOC chambers, their volume does not affect the partial pressure of the compound used. Small chambers can therefore be used, where moisture can be more easily removed from the chamber.

Table 1 compiles suitable metallo-organic compounds for use in MIVOC technology. When using the MIVOC method, it should be noted that a number of the reagents may be toxic, corrosive, hygroscopic or have other important properties. Therefore, it is recommended to always inform yourself about the recommended handling precautions of various substances before using them.

It should also be mentioned that the breakup of the molecules used produces larger quantities of hydrogen and carbon ions, which makes it difficult to set specific ion charge distributions in the ion source. Carbon also contaminates the source and thus leads to a reduction in the ion currents of the target element.

Table 1: Organometallic and other compounds for loading ion sources with metal ions. The table is based on a compilation by [Ullmann 2005], including various additions by the author. The specification of a compound without a literature reference means that the listed compound can potentially be used, but that the author is not aware of any literature work on it.

Z	name	sum formula	references
5	1,2-dicarbado-decaborane(12) also called decaborane(12)	$C_2H_{12}B_{10}$	[Bogomolov et al. 1999] [Koivisto et al. 2001] [Bogomolov et al. 2015] [Loginov et al. 2018]
	decaborane(14)	$B_{10}H_{14}$	[Oshiro et al. 2014]
12	magnesocene	$Mg(C_5H_5)_2$	[Koivisto et al. 1998] [Takasugi et al. 2010]
13	trimethyl aluminium	$AlC_3H_9$	
14	silicon tetrachloride	$SiCl_4$	[Takasugi et al. 2010]
	tetramethylsilane	$Si(CH_3)_4$	[Takasugi et al. 2010] [Bondarchenko et al. 2020]
	tetrakis(trimethyl-silyl)silane	$Si[(CH_3)_3Si]_4$	[Koivisto et al. 2002]
15	diethyl phosphite	$(C_2H_5O)_2P(O)H$	[Kentsch et al. 2004a]
22	titanium (IV) chloride	$TiCl_4$	[Kentsch et al. 2004] [Takasugi et al. 2010]
	titanium tetrafluoride	$TiF_4$	[Bogomolov et al 2014]
	cyclopentadienyl cycloheptatrienyl titanium	$C_5H_5TiC_7H_7$	[Bogomolov et al 2014]
	(trimethyl)pentamethyl cyclopentadienyl titanium(IV)	$(CH_3)_5C_5Ti(CH_3)_3$	[Bogomolov et al 2014] [Bondarchenko et al. 2020] [Pugachev et al. 2021]
	titanocene dichloride	$(C_5H_5)_2TiCl_2$	
	titanium (IV) ethylate	$Ti(OC_2H_5)_4$	
23	vanadocene	$V(C_5H_5)_2$	[Ullrich et al. 1998] [Bogomolov et al. 2015] [Bondarchenko et al. 2016]
24	chromozene	$Cr(C_5H_5)_2$	[Koivisto et al. 1998] [Bogomolov et al. 2015] [Bondarchenko et al. 2016] [Bondarchenko et al. 2020] [Pugachev et al. 2021]

Z	name	sum formula	references
	chromium hexacarbonyl	$\text{Cr}(\text{CO})_6$	[Koivisto et al. 1998] [Nakagawa et al. 1998]
25	methylcyclopentadienyl mangan-tricarbonyl	$\text{Mn}(\text{CH})_5\text{CH}_3(\text{CO})_3$	[Werner et al. 2000] [Kentsch et al. 2002a]
26	ferrocene	$\text{Fe}(\text{C}_5\text{H}_5)_2$	[Koivisto et al. 1994] [Stiebing et al. 1999] [Werner et al. 2000] [Kentsch et al. 2002] [Ullmann 2005] [Takasugi et al. 2010] [Bondarchenko et al. 2020] [Liu et al 2020]
27	cobaltocene	$\text{Co}(\text{C}_5\text{H}_5)_2$	[Koivisto et al. 1998] [Bogomolov et al. 2015] [Bondarchenko et al. 2016] [Bondarchenko et al. 2020] [Loginov et al. 2020]
	dicobalt octacarbony	$\text{Co}_2(\text{CO})_8$	[Koivisto et al. 2002]
	cyclopentadienyl-cobalt- dicarbonyl	$\text{CoC}_5\text{H}_5(\text{CO})_2$	
28	nickelocene	$\text{Ni}(\text{C}_5\text{H}_5)_2$	[Koivisto et al. 1994] [Stiebing et al. 1999] [Barue et al. 2000] [Kentsch et al. 2002a] [Kentsch et al. 2002] [Bogomolov et al. 2015] [Bondarchenko et al. 2016] [Bondarchenko et al. 2020] [Loginov et al. 2020]
29	copper (II) acetyl acetate	$\text{Cu}(\text{CH}_3\text{COCHCOCH}_3)_2$	
30	diethylzinc	$\text{Zn}(\text{C}_2\text{H}_5)_2$	[Kentsch et al. 2004]
	4-cyclohexylbutyric acid zinc salt	$\text{Zn}[\text{C}_6\text{H}_{11}(\text{CH}_2)_3\text{CO}_2]_2$	
31	trimethylgallium	$\text{GaC}_3\text{H}_9$	
	gallium (III) chloride	$\text{GaCl}_3$	

Z	name	sum formula	references
32	tetramethylgermanium	$\text{Ge}(\text{CH}_3)_4$	[Werner et al. 2000] [Bogomolov et al. 2015] [Bondarchenko et al. 2016] [Bondarchenko et al. 2020]
	tetramethylgermane	$\text{Ge}(\text{CH}_2\text{CH}_3)_4$	[Bogomolov et al. 2015] [Bondarchenko et al. 2016]
	dimethylgermane	$\text{Ge}(\text{CH}_3)_2\text{H}_2$	[Takasugi et al. 2010]
33	phenylarsine	$\text{As}(\text{C}_6\text{H}_5)\text{H}_2$	
	arsenic trioxide ethyl ester	$\text{As}(\text{C}_2\text{H}_5\text{O})_3$	
34	dimethylselenide	$\text{SeC}_2\text{H}_6$	
39	yttrium (III) isopropylate	$\text{Y}[(\text{CH}_3)_2\text{CHO}]_3$	
40	zirconocene dichloride	$(\text{C}_5\text{H}_5)_2\text{ZrCl}_2$	
41	niobium (V) ethylate	$\text{Nb}(\text{OC}_2\text{H}_5)_5$	
42	molybdenum hexacarbonyl	$\text{Mo}(\text{CO})_6$	[Koivisto et al. 1998] [Nakagawa et al. 1998]
44	ruthenocene	$\text{Ru}(\text{C}_5\text{H}_5)_2$	[Koivisto et al. 1998] [Nakagawa et al. 1998]
48	dimethylcadmium	$\text{C}_2\text{H}_6\text{Cd}$	
49	triethylindium	$(\text{C}_2\text{H}_5)_3\text{In}$	
	indium (III) tert-butylate	$[(\text{CH}_3)_3\text{CO}]_3\text{In}$	
50	Tetramethyltin	$(\text{CH}_3)_4\text{Sn}$	[Werner et al. 2000]
51	Trimethylantimon	$\text{C}_3\text{H}_9\text{Sb}$	[Nakamura et al. 2000]
	antimony (III) chloride	$\text{SbCl}_3$	
	triisopropyl antimony acid ester	$\text{Sb}[\text{OCH}(\text{CH}_3)_2]_3$	
52	dimethyltellurium	$\text{C}_2\text{H}_6\text{Te}$	[Nakamura et al. 2000]
53	diiodomethane	$\text{I}_2\text{CH}_2$	[Koivisto et al. 2002]
	diiodine	$\text{I}_2$	
59	tris(cyclopentadienyl) praseodymium	$(\text{C}_5\text{H}_5)_3\text{Pr}$	
60	neodymium (III) cyclo-pentadienylide	$(\text{C}_5\text{H}_5)_3\text{Nd}$	
65	terbium (III) acetyl acetonate hydrate	$[\text{CH}_3\text{COCH}=\text{C}(\text{O}-)C(\text{CH}_3)_3]_3\text{Tb}\cdot x\text{H}_2\text{O}$	



Z	name	sum formula	references
72	bis-(tert.-butylcyclopentadienyl)dimethyl hafnium	$C_{18}H_{26}Cl_2Hf$	
	dimethylbis(cyclopentadienyl)hafnium(IV)	$(C_5H_5)_2Hf(CH_3)_2$	[Jovovic et al. 2007] [Bogomolov et al. 2015] [Bondarchenko et al. 2016] [Bondarchenko et al. 2020]
74	tungsten hexacarbonyl	$W(CO)_6$	[ZiMin et al. 2000] [Koivisto et al. 2002]
76	osmocene	$Os(C_5H_5)_2$	[Koivisto et al. 1998] [Nakagawa et al. 1998] [Koivisto et al. 2002]
78	(cis,cis-1,5-Cyclooctadien)-dimethylplatin (II)	$C_{10}H_{18}Pt$	
83	bismuth (III) chloride	$BiCl_3$	
	triphenyl bismuth	$(C_6H_5)_3Bi$	
	bismuth(III)-2,2,6,6-tetramethyl-3,5-heptanedionate	$[(CH_3)_3CCOCH=C(O- )C(CH_3)_3]_3Bi$	

In combination with the MIVOC method, ion currents for charge state separated metal ions up to approx. some  $100 \mu A$  were achieved in ECRIS. For EBIS, DC currents up to a maximum of nA can be achieved for low ion charge states, for higher charged ions significantly less (about pA).

As examples, ion beam currents are tabulated in Table 2 as they were published in connection with the operation of EBIS and ECRIS. In the case of ECRIS, ion currents are specified in the DC mode, whereas pulsed or DC currents are specified for EBIS. The values measured for EBIS as DC currents were obtained in leaky mode, i.e. from a continuous ion current across the electrostatic trap potential.

Table 2: Ion currents during loading of ECRIS and EBIS with organometallic and other compounds. For the sake of compactness, the individual ECRIS and EBIS used are not characterized in detail and the operating parameters sets are not listed. However, the interested reader will find these in the original literature cited for each value. The specified ion currents are to be understood as electric particle currents, i.e. to determine the extracted ion numbers, the specified values must still be divided by the indicated ion charge state. Furthermore, it should be noted that the tabulated values are only orientation values. In some cases, the values were obtained from spectra in which the maximum extractable current was optimized for a specific ion charge state. Careful optimization can therefore lead to even higher ion currents for individual ion charge states. In the case of EBIS, "\*" is used to characterize ion currents measured in a pulsed EBIS regime. The abbreviation "Im" stands for leaky mode.

Z	ion	$I_i$	compound	source	references
5	$^{11}\text{B}^{1+}$	4 nA*	(H <sub>3</sub> CO) <sub>3</sub> B	EBIS	[Sasse 2012]
	$^{11}\text{B}^{1+}$	25 $\mu\text{A}$	C <sub>2</sub> H <sub>12</sub> B <sub>10</sub>	ECRIS	[Bogomolov et al. 2015]
	$^{11}\text{B}^{2+}$	2 nA*	(H <sub>3</sub> CO) <sub>3</sub> B	EBIS	[Sasse 2012]
	$^{11}\text{B}^{2+}$	70 $\mu\text{A}$	C <sub>2</sub> H <sub>12</sub> B <sub>10</sub>	ECRIS	[Bogomolov et al. 2015]
	$^{11}\text{B}^{3+}$	1 nA*	(H <sub>3</sub> CO) <sub>3</sub> B	EBIS	[Sasse 2012]
	$^{11}\text{B}^{3+}$	190 $\mu\text{A}$	C <sub>2</sub> H <sub>12</sub> B <sub>10</sub>	ECRIS	[Bogomolov et al. 2015]
	$^{11}\text{B}^{4+}$	200 pA*	(H <sub>3</sub> CO) <sub>3</sub> B	EBIS	[Sasse 2012]
	$^{11}\text{B}^{4+}$	85 $\mu\text{A}$	C <sub>2</sub> H <sub>12</sub> B <sub>10</sub>	ECRIS	[Bogomolov et al. 2015]
	$^{11}\text{B}^{5+}$	60 pA*	(H <sub>3</sub> CO) <sub>3</sub> B	EBIS	[Sasse 2012]
14	$^{28}\text{Si}^{5+}$	24 $\mu\text{A}$	Si(CH <sub>3</sub> ) <sub>4</sub>	ECRIS	[Loginov et al. 2020]
	$^{28}\text{Si}^{5+}$	62 $\mu\text{A}$	Si(CH <sub>3</sub> ) <sub>4</sub>	ECRIS	[Bondarchenko et al. 2020]
	$^{28}\text{Si}^{6+}$	40 $\mu\text{A}$	Si(CH <sub>3</sub> ) <sub>4</sub>	ECRIS	[Bondarchenko et al. 2020]
	Si <sup>8+</sup>	9 pA*	Si[Si(CH <sub>3</sub> ) <sub>3</sub> ] <sub>4</sub>	EBIS	[Ullmann 2005]
	Si <sup>10+</sup>	6 pA*	Si[Si(CH <sub>3</sub> ) <sub>3</sub> ] <sub>4</sub>	EBIS	[Ullmann 2005]
	Si <sup>11+</sup>	2 pA*	Si[Si(CH <sub>3</sub> ) <sub>3</sub> ] <sub>4</sub>	EBIS	[Ullmann 2005]
	Si <sup>12+</sup>	320 fA*	Si[Si(CH <sub>3</sub> ) <sub>3</sub> ] <sub>4</sub>	EBIS	[Ullmann 2005]
	Si <sup>13+</sup>	220 fA*	Si[Si(CH <sub>3</sub> ) <sub>3</sub> ] <sub>4</sub>	EBIS	[Ullmann 2005]
	Si <sup>14+</sup>	100 fA*	Si[Si(CH <sub>3</sub> ) <sub>3</sub> ] <sub>4</sub>	EBIS	[Ullmann 2005]
15	P <sup>11+</sup>	3 pA*	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)H	EBIS	[Kentsch et al. 2004a]
	P <sup>15+</sup>	255 fA*	(C <sub>2</sub> H <sub>5</sub> O) <sub>2</sub> P(O)H	EBIS	[Kentsch et al. 2004a]

Z	ion	$I_i$	compound	source	references
22	$^{48}\text{Ti}^{5+}$	79 $\mu\text{A}$	$\text{C}_5(\text{CH}_3)_5\text{Ti}(\text{CH}_3)_3$	ECRIS	[Bogomolov et al 2014]
	$^{50}\text{Ti}^{5+}$	82 $\mu\text{A}$	$\text{C}_5(\text{CH}_3)_5\text{Ti}(\text{CH}_3)_3$	ECRIS	[Bogomolov et al 2014]
	$^{48}\text{Ti}^{9+}$	18 $\mu\text{A}$	$\text{C}_5(\text{CH}_3)_5\text{Ti}(\text{CH}_3)_3$	ECRIS	[Bondarchenko et al. 2020]
	$^{48}\text{Ti}^{10+}$	20 $\mu\text{A}$	$\text{C}_5(\text{CH}_3)_5\text{Ti}(\text{CH}_3)_3$	ECRIS	[Jardin et al. 2012]
	$^{48}\text{Ti}^{10+}$	16 $\mu\text{A}$	$\text{C}_5(\text{CH}_3)_5\text{Ti}(\text{CH}_3)_3$	ECRIS	[Bondarchenko et al. 2020]
	$^{48}\text{Ti}^{11+}$	68 $\mu\text{A}$	$\text{C}_5(\text{CH}_3)_5\text{Ti}(\text{CH}_3)_3$	ECRIS	[Bogomolov et al 2014]
23	$\text{V}^{5+}$	75 $\mu\text{A}$	$\text{V}(\text{C}_5\text{H}_5)_2$	ECRIS	[Bondarchenko et al. 2016]
	$\text{V}^{6+}$	54 $\mu\text{A}$	$\text{V}(\text{C}_5\text{H}_5)_2$	ECRIS	[Bondarchenko et al. 2016]
	$\text{V}^{7+}$	41 $\mu\text{A}$	$\text{V}(\text{C}_5\text{H}_5)_2$	ECRIS	[Bondarchenko et al. 2016]
	$\text{V}^{8+}$	54 $\mu\text{A}$	$\text{V}(\text{C}_5\text{H}_5)_2$	ECRIS	[Bondarchenko et al. 2016]
	$\text{V}^{9+}$	55 $\mu\text{A}$	$\text{V}(\text{C}_5\text{H}_5)_2$	ECRIS	[Bondarchenko et al. 2016]
	$\text{V}^{10+}$	43 $\mu\text{A}$	$\text{V}(\text{C}_5\text{H}_5)_2$	ECRIS	[Bondarchenko et al. 2016]
	$\text{V}^{11+}$	34 $\mu\text{A}$	$\text{V}(\text{C}_5\text{H}_5)_2$	ECRIS	[Bondarchenko et al. 2016]
	$\text{V}^{12+}$	19 $\mu\text{A}$	$\text{V}(\text{C}_5\text{H}_5)_2$	ECRIS	[Bondarchenko et al. 2016]
24	$\text{Cr}^{5+}$	50 $\mu\text{A}$	$\text{Cr}(\text{C}_5\text{H}_5)_2$	ECRIS	[Bondarchenko et al. 2016]
	$\text{Cr}^{6+}$	70 $\mu\text{A}$	$\text{Cr}(\text{C}_5\text{H}_5)_2$	ECRIS	[Bondarchenko et al. 2016]
	$\text{Cr}^{7+}$	60 $\mu\text{A}$	$\text{Cr}(\text{C}_5\text{H}_5)_2$	ECRIS	[Bondarchenko et al. 2016]
	$\text{Cr}^{8+}$	37 $\mu\text{A}$	$\text{Cr}(\text{C}_5\text{H}_5)_2$	ECRIS	[Bondarchenko et al. 2016]
	$^{52}\text{Cr}^{8+}$	22 $\mu\text{A}$	$\text{Cr}(\text{C}_5\text{H}_5)_2$	ECRIS	[Bondarchenko et al. 2020]
	$\text{Cr}^{9+}$	17 $\mu\text{A}$	$\text{Cr}(\text{C}_5\text{H}_5)_2$	ECRIS	[Bondarchenko et al. 2016]
	$\text{Cr}^{10+}$	7 $\mu\text{A}$	$\text{Cr}(\text{C}_5\text{H}_5)_2$	ECRIS	[Bondarchenko et al. 2016]
	$^{52}\text{Cr}^{10+}$	9 $\mu\text{A}$	$\text{Cr}(\text{C}_5\text{H}_5)_2$	ECRIS	[Bondarchenko et al. 2020]
	$^{52}\text{Cr}^{10+}$	18 $\mu\text{A}$	$\text{Cr}(\text{C}_5\text{H}_5)_2$	ECRIS	[Loginov et al. 2020]
26	$\text{Fe}^{6+}$	43 $\mu\text{A}$	$\text{Fe}(\text{C}_5\text{H}_5)_2$	ECRIS	[Bondarchenko et al. 2016]
	$\text{Fe}^{6+}$	7 $\mu\text{A}^{lm}$	$\text{Fe}(\text{C}_5\text{H}_5)_2$	EBIS	[Sasse 2012]
	$\text{Fe}^{7+}$	93 $\mu\text{A}$	$\text{Fe}(\text{C}_5\text{H}_5)_2$	ECRIS	[Bondarchenko et al. 2016]
	$\text{Fe}^{8+}$	125 $\mu\text{A}$	$\text{Fe}(\text{C}_5\text{H}_5)_2$	ECRIS	[Bondarchenko et al. 2016]
	$^{56}\text{Fe}^{8+}$	68 $\mu\text{A}$	$\text{Fe}(\text{C}_5\text{H}_5)_2$	ECRIS	[Bondarchenko et al. 2020]
	$\text{Fe}^{9+}$	172 $\mu\text{A}$	$\text{Fe}(\text{C}_5\text{H}_5)_2$	ECRIS	[Bondarchenko et al. 2016]
	$\text{Fe}^{10+}$	145 $\mu\text{A}$	$\text{Fe}(\text{C}_5\text{H}_5)_2$	ECRIS	[Bondarchenko et al. 2016]
	$^{56}\text{Fe}^{10+}$	44 $\mu\text{A}$	$\text{Fe}(\text{C}_5\text{H}_5)_2$	ECRIS	[Bondarchenko et al. 2020]

Z	ion	$I_i$	compound	source	references
	Fe <sup>10+</sup>	2 $\mu A^{lm}$	Fe(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	EBIS	[Sasse 2012]
	Fe <sup>11+</sup>	114 $\mu A$	Fe(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	ECRIS	[Bondarchenko et al. 2016]
	<sup>56</sup> Fe <sup>11+</sup>	25 $\mu A$	Fe(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	ECRIS	[Bondarchenko et al. 2020]
	Fe <sup>12+</sup>	73 $\mu A$	Fe(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	ECRIS	[Bondarchenko et al. 2016]
	<sup>56</sup> Fe <sup>12+</sup>	12 $\mu A$	Fe(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	ECRIS	[Bondarchenko et al. 2020]
	Fe <sup>12+</sup>	800 pA <sup>lm</sup>	Fe(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	EBIS	[Sasse 2012]
	Fe <sup>13+</sup>	45 $\mu A$	Fe(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	ECRIS	[Bondarchenko et al. 2016]
	Fe <sup>17+</sup>	20 pA*	Fe(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	EBIS	[Sasse 2012]
	Fe <sup>17+</sup>	300 pA <sup>lm</sup>	Fe(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	EBIS	[Sasse 2012]
	Fe <sup>20+</sup>	100 pA <sup>lm</sup>	Fe(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	EBIS	[Sasse 2012]
	Fe <sup>24+</sup>	5 pA <sup>lm</sup>	Fe(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	EBIS	[Sasse 2012]
	Fe <sup>25+</sup>	200 fA <sup>lm</sup>	Fe(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	EBIS	[Sasse 2012]
	Fe <sup>25+</sup>	625 fA*	Fe(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	EBIS	[Sasse 2012]
	Fe <sup>26+</sup>	520 fA*	Fe(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	EBIS	[Sasse 2012]
27	Co <sup>6+</sup>	57 $\mu A$	Co(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	ECRIS	[Bondarchenko et al. 2016]
	Co <sup>7+</sup>	80 $\mu A$	Co(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	ECRIS	[Bondarchenko et al. 2016]
	Co <sup>8+</sup>	86 $\mu A$	Co(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	ECRIS	[Bondarchenko et al. 2016]
	Co <sup>9+</sup>	98 $\mu A$	Co(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	ECRIS	[Bondarchenko et al. 2016]
	<sup>59</sup> Co <sup>9+</sup>	57 $\mu A$	Co(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	ECRIS	[Bondarchenko et al. 2020]
	<sup>59</sup> Co <sup>10+</sup>	73 $\mu A$	Co(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	ECRIS	[Bondarchenko et al. 2020]
	Co <sup>11+</sup>	82 $\mu A$	Co(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	ECRIS	[Bondarchenko et al. 2016]
	<sup>59</sup> Co <sup>11+</sup>	36 $\mu A$	Co(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	ECRIS	[Bondarchenko et al. 2020]
	Co <sup>12+</sup>	25 $\mu A$	Co(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	ECRIS	[Bondarchenko et al. 2016]
	<sup>59</sup> Co <sup>12+</sup>	12 $\mu A$	Co(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	ECRIS	[Bondarchenko et al. 2020]
	<sup>59</sup> Co <sup>12+</sup>	12 $\mu A$	Co(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	ECRIS	[Loginov et al. 2020]
28	Ni <sup>6+</sup>	45 $\mu A$	Ni(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	ECRIS	[Bondarchenko et al. 2016]
	Ni <sup>7+</sup>	43 $\mu A$	Ni(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	ECRIS	[Bondarchenko et al. 2016]
	Ni <sup>8+</sup>	48 $\mu A$	Ni(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	ECRIS	[Bondarchenko et al. 2016]
	Ni <sup>9+</sup>	53 $\mu A$	Ni(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	ECRIS	[Bondarchenko et al. 2016]
	<sup>58</sup> Ni <sup>9+</sup>	39 $\mu A$	Ni(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	ECRIS	[Bondarchenko et al. 2020]
	Ni <sup>11+</sup>	30 $\mu A$	Ni(C <sub>5</sub> H <sub>5</sub> ) <sub>2</sub>	ECRIS	[Bondarchenko et al. 2016]

Z	ion	$I_i$	compound	source	references
	$^{58}\text{Ni}^{11+}$	43 $\mu\text{A}$	$\text{Ni}(\text{C}_5\text{H}_5)_2$	ECRIS	[Bondarchenko et al. 2020]
	$^{58}\text{Ni}^{11+}$	43 $\mu\text{A}$	$\text{Ni}(\text{C}_5\text{H}_5)_2$	ECRIS	[Loginov et al. 2020]
	$\text{Ni}^{12+}$	10 $\mu\text{A}$	$\text{Ni}(\text{C}_5\text{H}_5)_2$	ECRIS	[Bondarchenko et al. 2016]
	$^{58}\text{Ni}^{12+}$	37 $\mu\text{A}$	$\text{Ni}(\text{C}_5\text{H}_5)_2$	ECRIS	[Bondarchenko et al. 2020]
	$^{58}\text{Ni}^{12+}$	9 $\mu\text{A}$	$\text{Ni}(\text{C}_5\text{H}_5)_2$	ECRIS	[Koivisto et al. 1998]
	$^{58}\text{Ni}^{13+}$	6 $\mu\text{A}$	$\text{Ni}(\text{C}_5\text{H}_5)_2$	ECRIS	[Koivisto et al. 1998]
	$^{58}\text{Ni}^{14+}$	3 $\mu\text{A}$	$\text{Ni}(\text{C}_5\text{H}_5)_2$	ECRIS	[Koivisto et al. 1998]
	$^{58}\text{Ni}^{15+}$	1 $\mu\text{A}$	$\text{Ni}(\text{C}_5\text{H}_5)_2$	ECRIS	[Koivisto et al. 1998]
32	$\text{Ge}^{7+}$	43 $\mu\text{A}$	$\text{Ge}(\text{CH}_2\text{CH}_3)_4$ $\text{Ge}(\text{CH}_3)_4$	ECRIS	[Bondarchenko et al. 2016]
	$\text{Ge}^{8+}$	54 $\mu\text{A}$	$\text{Ge}(\text{CH}_2\text{CH}_3)_4$ $\text{Ge}(\text{CH}_3)_4$	ECRIS	[Bondarchenko et al. 2016]
	$^{72}\text{Ge}^{8+}$	38 $\mu\text{A}$	$\text{Ge}(\text{CH}_3)_4$	ECRIS	[Bondarchenko et al. 2020]
	$\text{Ge}^{10+}$	47 $\mu\text{A}$	$\text{Ge}(\text{CH}_2\text{CH}_3)_4$ $\text{Ge}(\text{CH}_3)_4$	ECRIS	[Bondarchenko et al. 2016]
	$^{72}\text{Ge}^{10+}$	46 $\mu\text{A}$	$\text{Ge}(\text{CH}_3)_4$	ECRIS	[Bondarchenko et al. 2020]
	$^{72}\text{Ge}^{11+}$	34 $\mu\text{A}$	$\text{Ge}(\text{CH}_3)_4$	ECRIS	[Bondarchenko et al. 2020]
72	$\text{Hf}^{13+}$	31 $\mu\text{A}$	$(\text{C}_5\text{H}_5)_2\text{Hf}(\text{CH}_3)_2$	ECRIS	[Bondarchenko et al. 2016]
	$\text{Hf}^{14+}$	45 $\mu\text{A}$	$(\text{C}_5\text{H}_5)_2\text{Hf}(\text{CH}_3)_2$	ECRIS	[Bondarchenko et al. 2016]
	$\text{Hf}^{16+}$	50 $\mu\text{A}$	$(\text{C}_5\text{H}_5)_2\text{Hf}(\text{CH}_3)_2$	ECRIS	[Bondarchenko et al. 2016]
	$\text{Hf}^{17+}$	45 $\mu\text{A}$	$(\text{C}_5\text{H}_5)_2\text{Hf}(\text{CH}_3)_2$	ECRIS	[Bondarchenko et al. 2016]
	$^{180}\text{Hf}^{17+}$	19 $\mu\text{A}$	$(\text{C}_5\text{H}_5)_2\text{Hf}(\text{CH}_3)_2$	ECRIS	[Bondarchenko et al. 2020]
	$\text{Hf}^{18+}$	36 $\mu\text{A}$	$(\text{C}_5\text{H}_5)_2\text{Hf}(\text{CH}_3)_2$	ECRIS	[Bondarchenko et al. 2016]
	$^{180}\text{Hf}^{18+}$	15 $\mu\text{A}$	$(\text{C}_5\text{H}_5)_2\text{Hf}(\text{CH}_3)_2$	ECRIS	[Bondarchenko et al. 2020]
	$\text{Hf}^{19+}$	27 $\mu\text{A}$	$(\text{C}_5\text{H}_5)_2\text{Hf}(\text{CH}_3)_2$	ECRIS	[Bondarchenko et al. 2016]
	$\text{Hf}^{20+}$	17 $\mu\text{A}$	$(\text{C}_5\text{H}_5)_2\text{Hf}(\text{CH}_3)_2$	ECRIS	[Bondarchenko et al. 2016]
	$^{180}\text{Hf}^{20+}$	5 $\mu\text{A}$	$(\text{C}_5\text{H}_5)_2\text{Hf}(\text{CH}_3)_2$	ECRIS	[Bondarchenko et al. 2020]
80	$^{202}\text{Hg}^{24+}$	20 pA*	Hg	EBIS	[Sasse 2012]
	$^{202}\text{Hg}^{33+}$	9 pA*	Hg	EBIS	[Sasse 2012]
	$^{202}\text{Hg}^{43+}$	4 pA*	Hg	EBIS	[Sasse 2012]
	$^{202}\text{Hg}^{51+}$	1 pA*	Hg	EBIS	[Sasse 2012]
	$^{202}\text{Hg}^{55+}$	152 fA*	Hg	EBIS	[Sasse 2012]

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Z	ion	$I_i$	compound	source	references
	Hg <sup>58+</sup>	70 fA*	Hg	EBIS	[Sasse 2012]

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