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RELATIVE SENSITIVITY COEFFICIENTS IN SPARK SOURCE MASS SPECTROMETRY (SSMS) OF METALS

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BUDAPEST

RELATIVE SENSITIVITY COEFFICIENTS IN
SPARK SOURCE MASS SPECTROMETRY (SSMS)
OF METALS

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ABSTRACT

Relative Sensitivity Coefficients (RSC) in aluminium, copper and iron using SSMS were determined with deep cooled electrodes. A straight line dependence was observed between log RSC and the boiling points of the impurities. The experimental results clearly indicate the importance of the relative heat of sublimation of the impurities.

АННОТАЦИЯ

Методом искровой масс-спектроскопии определены коэффициенты относительной чувствительности /КОЧ/ в алюминии, меди и стали. Найдена прямая зависимость между логарифмами КОЧ и температурами кипения примесей. Экспериментальные данные свидетельствуют об определяющей роли относительной энтальпии сублимации примесей в образовании КОЧ.

KIVONAT

Szikraforrás tömegspektroszkópiai analizis során fellépő relativ érzékenységi együtthatókat határoztunk meg aluminiumban, rézben és acélban mélyen hütött elektródokkal. Azt találtuk, hogy a relativ érzékenységi együtthatók logaritmusa a szennyezők forráspontjának lineáris függvénye. A kisérleti adatokból következtetni lehet a relativ szublimációs hő meghatározó szerepére a relativ érzékenységi együtthatók kialakulásában.

INTRODUCTION

Spark source mass spectrometry is a powerful analytical method for the trace impurity determination of metals and alloys but the quantification of data remains a real problem. Although quite a number of papers have dealt with this problem, the conclusions are by no means unanimous. It is generally accepted that by standardizing sparking conditions, i.e. the pulse length and frequency (repetition rate), spark voltage and source geometry, the standard deviation does not exceed 10-30 rel.%. In favourable cases and using appropriate standards the inaccuracy does not exceed this value either but sometimes reaches 100% or more. The reason is that constant readings of sparking parameters do not always result in the same sparking conditions. It is the energy consumed in the spark that influences most the condition of the plasma [1] and this energy is related to the true breakdown voltage [2], which is on the other hand a function of the electrode gap. This is why the relative sensitivities for different elements change according to the electrode gap [3]. From the works cited above and also from earlier ones [4,5,6,7] it is not too difficult to understand the variation of the relative sensitivities found in the literature (for a compilation, see ref.[8]), but one cannot understand completely why they differ from 1.

Van Hoye et al. [9] found that the ion energy distribution in the spark is similar - in fact almost identical - for all elements and no significant discrimination occurs either in the electrostatic analyser or in the magnetic field. So the reason for not having identical sensitivities for all elements is not in the ion optical system. Honig [10], Vidal et al. [11] and lately Shelpakova et al. [2] stated that the relative sensitivities would show a direct correlation with the ionization cross sections. According to our experiences however, this is generally not the case - at least not with highly dilute metals.

We fully accept that without considering the electrical parameters of plasma the ionizing processes cannot be understood and controlled [2]; at the same time, however, we believe that for a better understanding of relative sensitivities the condition of the sample as a macroscopic system should also be taken into account.

Halliday et al. [12] found large variations in relative sensitivities for impurities in steel when the repetition rate - i.e. the temperature of the electrodes - was drastically changed. This finding has not always been reported [13]. Owens and Giardino [14] Addink [15,16] and Honig [10] were the first to indicate the importance of the electrode temperature for the relative sensitivity coefficients (RSC). Throughout this paper the following definition of RSC will be used: $RSC = \dfrac{x/y_m}{x/y_{tr}}$ where x/y_m is the ratio of the concentrations of elements x and y as determined from single charged ions and x/y_{tr} is that of the true concentration. A standardized electrode temperature can be reached by cooling the electrodes - as was first indicated by Nyáry et al.[17] and recently demonstrated in detail by Van Hoye et al. [18].

In this report we will present RSC values obtained experimentally and we will discuss their dependence on the boiling points of the impurities.

EXPERIMENTAL

The measurements were carried out on an MS-702/R (AEI) mass spectrometer with Ilford Q-2 thin glass photoplate ion detection. The photoplate development was carried out with an ID-19 developer using the manufacturer's recommended figures of 20 $^{\circ}$C and three minutes in each case; the blackening of the lines was measured by a modified type G-II microdensitometer (Carl Zeiss, Jena, GDR). Two 1x1x10 mm pieces were prepared from the bulk, and after degreasing in acetone and washing with twice-distilled water they were put into the ion source. When the required vacuum was reached, the samples were presparked for one minute on each side with a pulse length of 200 μs at a repetition rate of 300 Hz. Then the

cold finger was filled with liquid nitrogen and after 20 minutes
waiting time we started aparking. The electrode cooling was ac-
complished by connecting the electrodes via braided copper wire
to the cold finger. The samples were arranged so that they faced
each other.

The measuring parameters were as follows:

Spark voltage	30 kV
Pulse length	100 μs
Repetition rate	100 Hz
Accelerating voltage	22 kV
Magnet current	230 mA
Pressure in the source	$\sim 2.10^{-5}$ Pa.

Graded exposures were taken and the quasi-linear part of the
blackening-log exposure (nC) curve was used for evaluation. Nei-
ther the multiply charged nor the polyatomic ions were taken
into consideration.

RESULTS AND DISCUSSION

Table I gives the RSC values obtained for the standard
samples JM-CA 4 and CC 2 copper, Alcan Series 15010-1 aluminium
and low alloy steel NBS-661. The values for impurities in the
aluminium standard were collected over a period of five years,
those for copper and iron standards are averages for ten separate
measurements. The overall precision is about 20% (rel.). The
silicion in iron was not determined because of line interferences.
In aluminium and iron the internal standard was iron, in copper
we used chromium. The results obtained were subsequently normal-
ized to chromium because it was present in all three samples.
This is the reason why the value for iron in the iron standard
equals 0.8 instead of 1.

The data obtained by us in aluminium agree reasonably well
with those Yamaguchi and Suzuki [19] and the RSC values for the
iron matrix with those obtained by McCrea [20] and Konishi [21].
Data obtained by Van Hoye et al. [18] for an aluminium matrix,

with a spark-source voltage of 30 kV and a repetition rate of
1 kHz and cooled electrodes agree quite well with ours apart from
zinc magnesium and titanium.

From the data of ref. [18] it can be seen that the cooling
of electrodes decreases the RSC values, especially those of the
elements with low boiling points (As, Sb, Mn, Sn, Zn, Mg, Pb) and
it has practically no effect (or at least less) on the values of
elements with higher boiling points (Si, Cu, Cr, Ni, Fe, Ti, V,
Nb, Co).

The alkali and alkali earth elements also become "measur-
able" by electrode cooling. Dietze [22] obtained a constant ion
beam for sodium in an aluminium matrix after 30 minutes of
presparking and found an RSC value of ~60. Table I clearly shows
the decrease of RSC's for this and also for other alkali elements
as a result of electrode cooling.

In *Fig. 1* the log RSC values obtained for an aluminium and
copper matrix, in *Fig. 2* those for an iron matrix are plotted
against the boiling points of the impurities. Trial fits of the
RSC values for the copper and aluminium matrices showed that no
significant differences in least squares parameters occur there-
fore the data were fitted together to a common line. The equa-
tions of the straight lines are given in the figures. The slope
of the straight line for the iron matrix is similar to that of
aluminium, expecially if the elements with high boiling points,
not present in aluminium, were omitted. If the data of Van Hoye
et al. were to be plotted they would show a similar character
(see Table 5 in [18]).

The RSC's for the alkali and alkali earth elements fall on
a separate straight line whose slope is much greater than that
of the line for other elements. This may be due to some surface
ionization.

The results can qualitatively be explained by the mechanism
proposed by Addink [15,16]. According to his theory, elements
with boiling points lower than that of the matrix can addition-
ally evaporate from an "additional zone [2]" to the actual "spark
zone [1]" where the evaporation of the material occurs. The size
of zone [2] is different for different impurities; greater for
elements of lower and smaller for elements of higher boiling

points, and it changes during sparking according to the heat
transferred instantaneously to the electrode. Using deep cooled
electrodes the size of zone [2] and the effect of additional
vaporization decreases and the RSC's approach 1, and the relative
heat of sublimation $(\Delta H)_r$, becomes the dominant factor influenc-
ing the RSC's. (ΔH_r) represents the standard enthalpy of sublima-
tion from bulk to mono-atomic state of the internal standard
divided by that of the element (impurity). This is supported by
*Fig. 3** where the relative heat of sublimation is plotted against
the boiling points of the impurities. The straight line has a
similar slope to those of *Fig. 1* and *Fig. 2*.

This may be taken as a justification for "substitution" of
$(\Delta H)_r$ values for the RSC values as a first approximation. It
emphasizes the governing role of the sublimation heat in the
ionization process during sparking. In constructing the straight
line the sublimation heats (from bulk to the atomic state) for
the elements arsenic, phosphorus, sulphur and selenium were not
taken into account because of the uncertainty as to which atomic
state is present in the gaseous phase. It can be seen however,
that the values obtained by using the heats of sublimation into
polyatomic states (probably S_2, Se_4, P_2, etc., see for example [23])
would fall on the straight line.

There is another interesting point which should be mentioned.
The (ΔH_r) values for alkalis and alkali earths also fall on the
straight line; this suggests that with more effective cooling the
RSC values for alkalis and alkali earths may decrease further.

Goshgarian and Jensen [24] proposed that use be made of the
heat of sublimation (ΔH), the atomic area, the ionization poten-
tial, and the isotopic masses of the elements in the calculation
of RSC's. Honig [10] suggested the use - apart from the heat of
sublimation - of the atomic areas and the ionization cross section
(sum of valence electrons, weighted by their mean square radii)

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*The heat of sublimation values are from the book "Energii razryva
khimicheskikh sviazei. Potencialy ionizatsii i srodstvo k elek-
tronu", Kondrat'ev V.N., Nauka, Moscow, 1974; the boiling points
from "Handbook of Chemistry and Physics" 52nd Edition, 1971-72,
Ed.: R.C. Weast, The Chemical Rubber Co., Cranwood Parkway,
Cleveland, Ohio, USA.

and he neglected the ionization potential on the basis of theoretical considerations. The importance of the ionization cross section has lately been proposed also in [2].

We also tried these methods and we concluded that in some cases the agreement between the calculated and the experimentally found RSC's is good; in others, however, it is very poor. This does not necessarily mean that the ionization potential, ionization cross section or other microscopic parameters, do not play any role in the initiation of the ion beam [8,25], but it probably does indicate that the approach used so far in the literature to describe the ionization processes in the spark is not complete (e.g. see Table 1 in [26]). Probably another approach leading to an understanding of the spark source ionization process would be more suitable. This would start with a fully ionized state that occurs during the first breakdown of the high voltage, and the final charge distribution between the different ionized states and elements would be the result of the ion recombination processes during the expansion of the plasma, as has also been pointed out recently by Ramend'ik [27].

We consider our results to be mainly of practical importance. Once the RSC values for some impurities in a matrix have been determined, those for the others can be estimated with reasonable confidence from the log RSC - boiling point straight line dependence. Even though we have analysed only three matrices (or rather only two) on the basis of known results (our own and those from the literature), we are inclined to the view that a significant matrix effect in conductive dilute metallic samples is not expected.

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Table 1

Experimentally found RSC values in aluminium,
copper and iron standards

	RSC (±~20% rel.)		
	Aluminium (Alcan 15010-1)	Copper (IM-CA 4; CC 2)	Iron (NBS-661)
P		3.0	3.0
S			2.5
As		3.0	3.5
Se			3.0
K	15.0		
Na	11.2		
Zn	3.5	3.5	
Mg	6.4		
Ca	4.0		
Bi	1.8	1.6	1.8
Pb	1.8	1.4	1.6
Sb	1.8	1.5	1.4
Mn	1.3		1.4
Ag		1.5	1.5
Sn	1.4	1.3	1.1
Si	1.0		1.0
B			0.6
Cu	0.8		1.1
Cr	1.1	1.1	1.1
Ni	0.7		0.6
Fe	1.0	1.0	0.8
Co			0.6
Ti	0.8		1.2
Co			0.8
V	0.6		1.0
La			1.5
Zr			0.8
Mo			0.5
Nb			0.4
Ta			0.3
W			0.23

$$RSC = 93{,}2\,e^{-1{,}8\,10^{-3}\,K}$$

$$RSC = 4{,}6\,e^{-5{,}2\,10^{-4}\,K}$$

● Al matrix
+ Cu matrix

RSC

10

1

K
Na
Mg
Ca

P
As
Zn

Sb Mn
Sn
Cr. Fe
Ti
V
Bi
Pb
Ag
Si
Cu
Ni

1000   2000   3000   4000
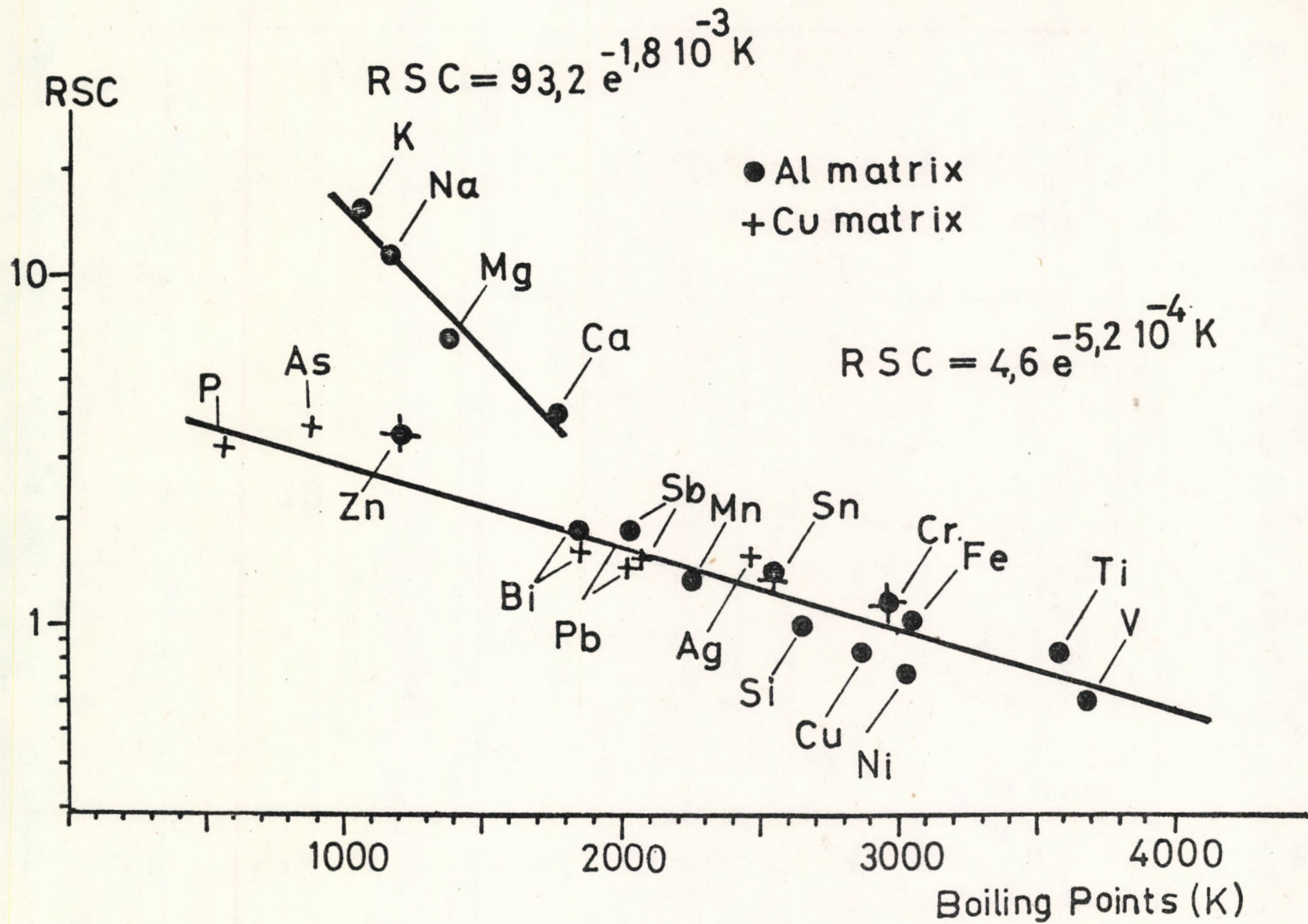
Boiling Points (K)

Fig. 1. Dependence of experimental RSC values on boiling points in
aluminium and copper matrices
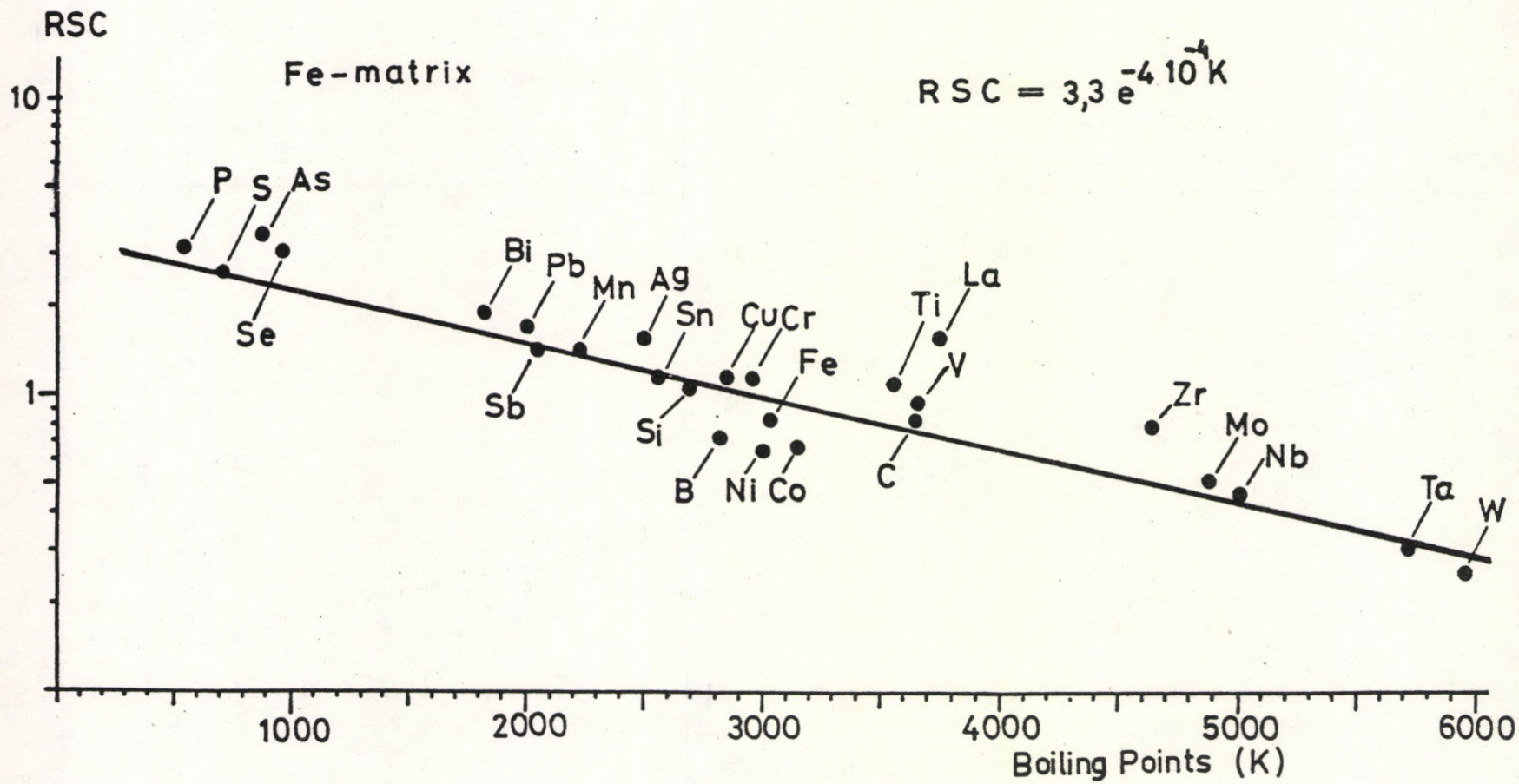
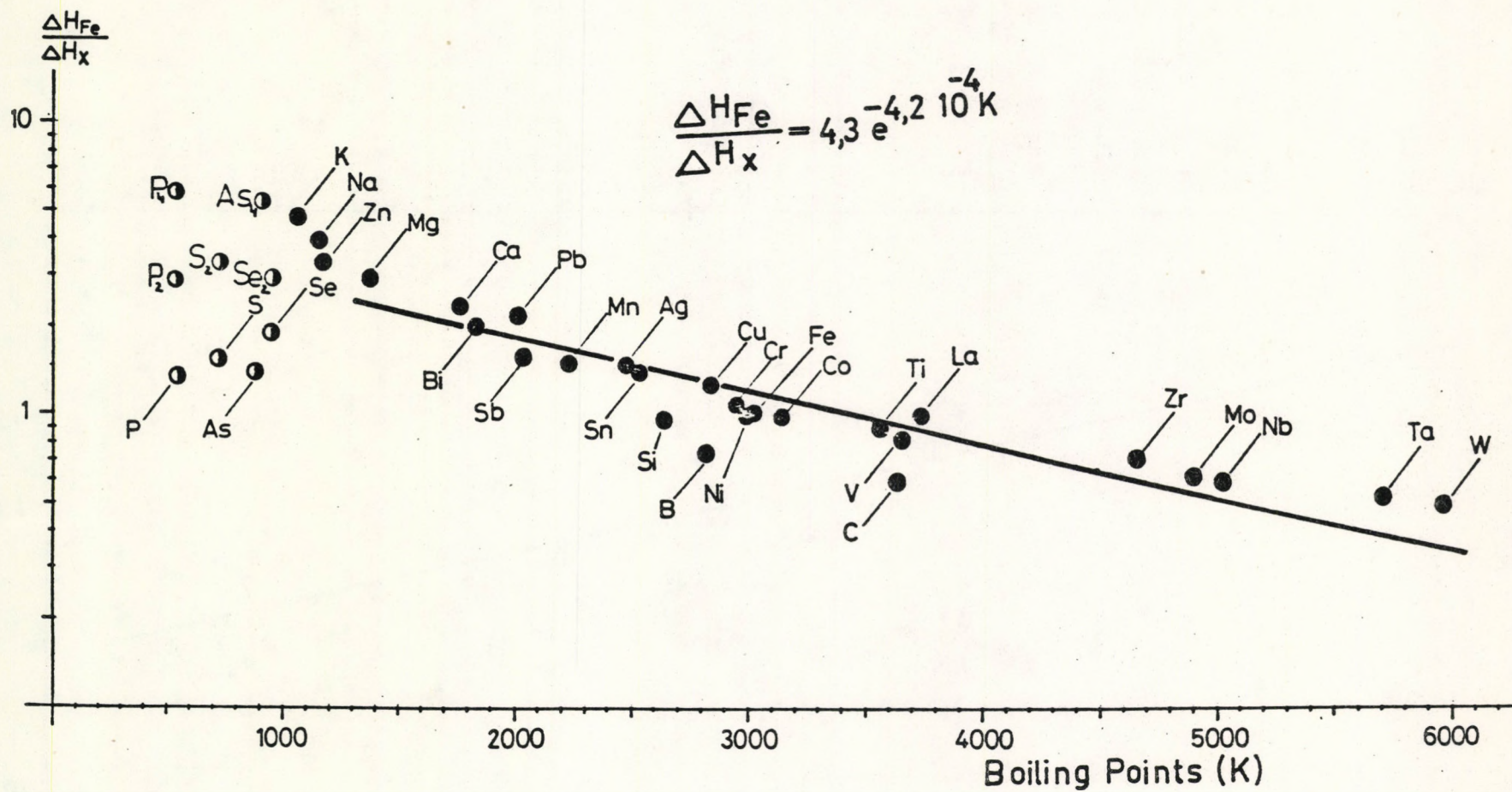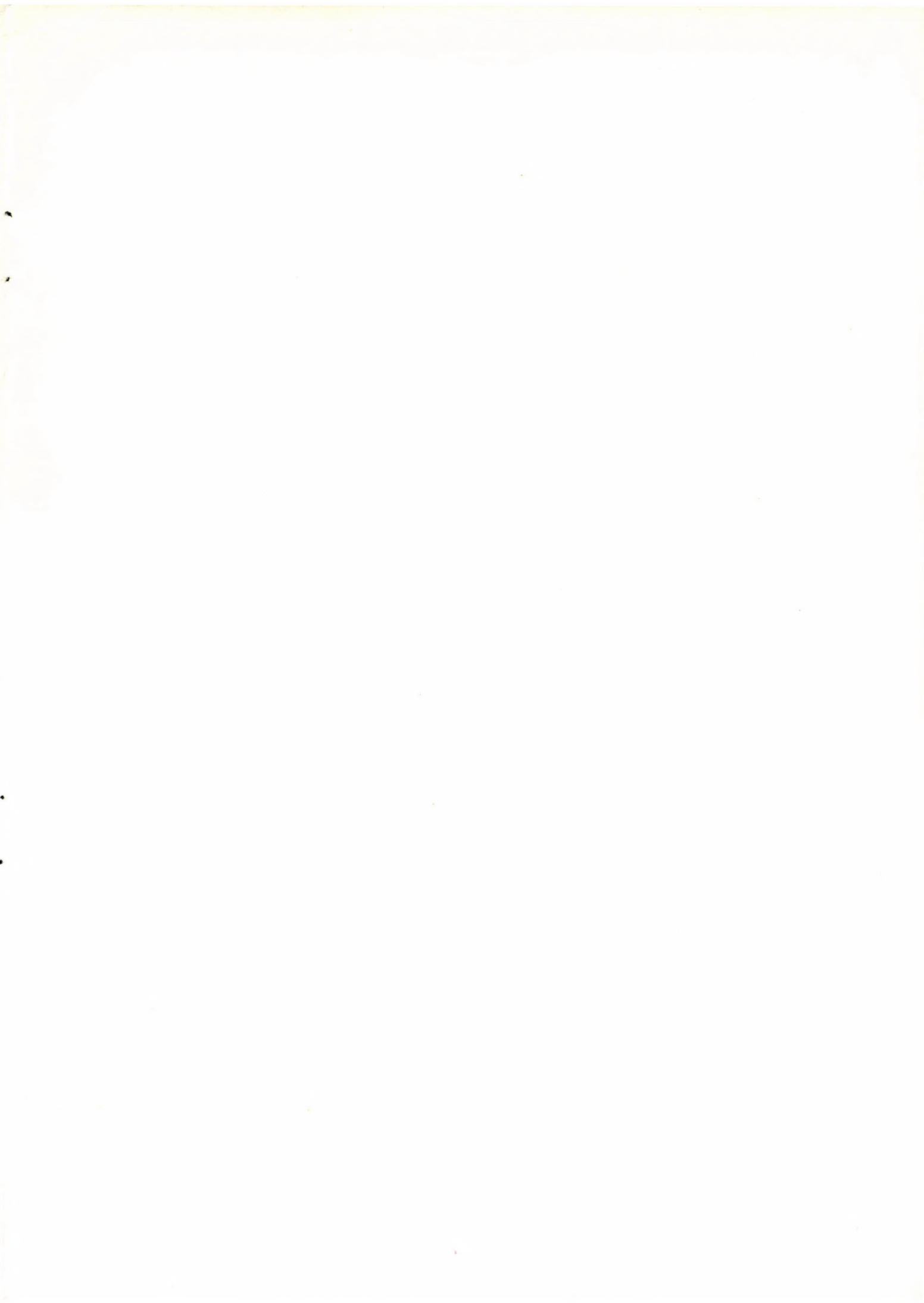Fig.2. Dependence of experimental RSC values on boiling points in iron matrix

$$\frac{\Delta H_{Fe}}{\Delta H_x} = 4,3\ e^{-4,2\ 10^{-4} K}$$

Fig.3. Plot of relative sublimation heats against boiling points

63.123