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Improvements in IRMS by ion current stabilization

Metody poprawiania stabilności prądów jonowych w spektrometrach mas
do pomiaru stosunków izotopowych

ABSTRACT

Practical methods of improving the ion current stability in Isotope Ratio Mass Spectrometry (IRMS) are presented. Instabilities generated by the collector assembly and antidy-natron voltage are discussed briefly. A simple method of indicating the magnetic field instabilities and measurement of m/e ratio directly is given. Also the well tested practical methods of cleaning of the ion source are described. Problems of stabilization of electron emission current and stabilization of filament temperature are discussed in relevance to ion current stability. Finally, the integration of ion currents is proposed as a replacement for the widely used high-ohm resistor amplifiers. Presented methods, designed and tested by the authors, are of importance for high-quality isotope ratio measurements.

1. INTRODUCTION

The quality of isotopic ratios measurement primarily depends on the stability of the ion currents. In this chapter we discuss the most typical sources of the instability of the ion beams. At the beginning we will assume that vacuum conditions are good and the magnetic analyzer (this refers to an

electromagnet) produces constant field while the high voltage supplied to the ion source is stable. When both conditions are fulfilled simultaneously a stable position of the ion beams with respect to the collector slits is achieved. Consequently, the average ion current may be constant over a long period of time. Fluctuations of the ion current of the beams having stable positions *versus* collector system are usually generated in the ion source. It is characteristic in this case that the fluctuations observed on any pair of the Faraday cups are correlated. If this is not the case, then most likely the reason of ion current variations may be unstable electron beam (in gas ion sources with electron impact ionization) or unstable filament temperature (in thermal ionization sources). These two sources of the ion beam instability can be nearly completely removed by the methods described in sections 5 and 6. Fluctuations of the ion current of the beams having stable positions *versus* collector system are usually generated in the ion source. It is characteristic in this case that the fluctuations observed on any pair of the Faraday cups are correlated.

One can easily recognize whether the ion beams fluctuate due to instabilities of high voltage and/or magnetic field or due to variation of the ion production rate. To test this one can set the major beam at the edge of the collector slit in the position at which the ion current drops to about half of its maximum value. If the stability of the ion current is apparently worse at this position than at the peak *plateau*, the reason of the observed fluctuation is the insufficient stability of the high voltage supply or the electromagnet power supply (if no permanent magnet is employed). This may be tested by precise measurement of a portion of the high voltage (between the ground and a selected point on the high voltage divider). A precision digital voltmeter (DVM) is necessary for this test. If DVM indicates high voltage fluctuations on the ion source, then one should test the high voltage supply after disconnecting it from the ion source. If the fluctuations disappear, then the cleaning of the ion source is mandatory (see section 4).

The instability of the magnetic field of the analyzer can be detected either by precision measurement of the electromagnet current or by the observation of the m/e indicator which displays a value proportional to square of

the magnetic field (B^2). Simple, but precise m/e indicators are described in section 3.

2. INSTABILITIES GENERATED IN THE COLLECTOR ASSEMBLY

Although the collector assembly of any IRMS is installed inside the high vacuum system, it can be troublesome when a noise is generated by spurious leaks of the ion currents to the ground. Usually the Faraday cups are mounted on high quality ceramics and they are directly connected through the leads of vacuum feedthroughs to the inputs of the amplifiers. These electric leaks are due to presence of various kinds of impurities on the collector ceramics and feedthroughs insulator. Another reason of correlated noise in all the Faraday cups can be due to unstable antidynatron voltage which is supplied to a common electrode installed in the collector assembly for repelling the secondary electrons. Such noise can be observed without ion beams!

The secondary electrons are produced by high energy ion beams when they pass along the collector slits and also when they fall into the cups. Without any suppressing voltage, i.e. when the antidynatron grid is firmly grounded, one can observe characteristic negative peaks (valleys) adjacent to each positive peak. These valleys are caused by electrons ejected from the edges of the collector slits. Because the voltage at the antidynatron grid should be extremely stable, it is advised to replace any electronic unit (DC supply) by a battery which can be simply arranged from 4 to 6 commercially available 9V batteries. The batteries should be closed in a grounded box and the negative potential of -40V to -60V (depending on the high voltage applied to the ion source) should be connected to the antidynatron grid by a shielded cable. In parallel to the output voltage, a high-quality capacitor of 1 to 10 μF is recommended for better voltage stability.

The above recommendation refers to older types of spectrometers having the antidynatron grid installed in the collector system. The modern machines have a permanent magnet installed for bending off the secondary electron trajectories. A small magnet is able to bend the trajectories of the electrons, but not the ion beams being composed of high energy massive particles.

In order to test the insulation quality one should observe (record) the noise of the amplifiers on the most sensitive ranges, i.e. at the same conditions as for their zero-setting. Then the amplifiers are set to the most rough range and their inputs are disconnected from the collector feedthroughs. Subsequently, the amplifier box is closed, or firmly shielded, and the zero-lines are recorded again on the most sensitive ranges. If an essential improvement is observed in this case in terms of lowering of the noise amplitude, then one has to clean the insulating surfaces. Obviously, the accessible surfaces (outside the high vacuum system) should be cleaned as first by washing them with ethyl alcohol and drying. Then the above test is repeated. If the enhanced noise is still observed, then prior to eventual cleaning of the collector assembly and inner surfaces of the feedthroughs, a uniform heating (up to ca. 100°C) of the flange with the collector assembly is recommended. In most cases such heating performed for a long period (e.g. overnight) significantly reduces the noise due to impurities on the inner insulating surfaces. *Nota bene* it is a good praxis to keep this part of the vacuum chamber always warm, at 50°C to 60°C except for the measurement time.

In the worst case, when the electric leaks are detected after thorough heating of the flange with the collector assembly, one has to clean the collectors after venting the analyzer tube. The best method of cleaning of the ceramic spacers is an acid treatment (HCl, HF) followed by boiling twice in distilled water, drying and baking in a quartz tube furnace at 600°C in open air. Deposits on the metallic parts of the collector assembly can be cleaned in the similar manner as the lenses of the ion source (see section 4).

3. m/e INDICATOR

A device precisely displaying the m/e ratio of a selected ion beam is extremely useful not only for identification of impurities in the background of a mass spectrum and in the adjustment of the distance between collector slits, but also in detection of instabilities of the magnetic field produced by an electromagnet. The reason of spatial instability of the ion beam can be

easily recognized by use of the m/e indicator which has a short-term precision at least 0.01 mass unit.

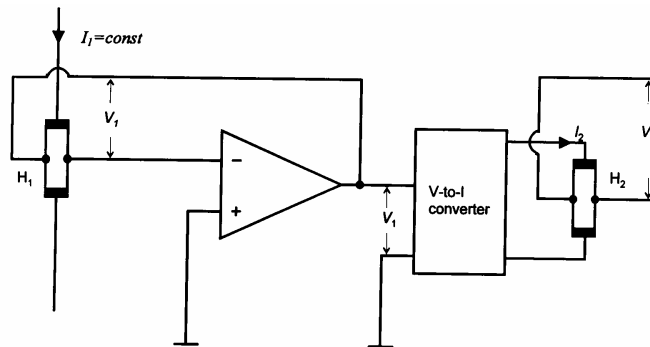


Fig.1. Schematic diagram of the two Hall probe method
Schemat obwodu z dwoma hallotronami

Hałas and Sikora (1987) described a simple dual Hall-probe device which indicates m/e ratio with the required short-term precision of 0.01 mass unit. The principle of its action is as follows. The first Hall probe, H_1 in Figure 1, is fed by a constant current I_1 . Thus the output voltage, V_1 , is proportional to the product

$$V_1 \sim I_1 B, \quad (1)$$

where B is the magnetic field intensity experienced by this Hall probe. The output voltage V_1 is repeated by the operational amplifier with 100% feedback coupling. The second Hall probe, H_2 , is fed by current I_2 directly proportional to V_1 from a voltage-to-current converter. If the second Hall probe experiences the same magnetic field, then its output signal, V_2 , will be proportional to the product $I_2 B$. Then, from (1) and the proportionality of I_2 to V_1 we obtain that

$$V_2 \sim B^2, \quad (2)$$

which means that V_2 will be proportional to the m/e value in the magnetic scanning operation mode.

By adjustment of the I_1 value, one can obtain the voltage V_2 (in millivolts) exactly equal to the actual m/e ratio, which is very useful. Two small electrically insulated Hall probes may be placed in parallel between the magnet poles to fulfill exactly the requirement of identity of the magnetic field intensities. In this m/e indicator two inexpensive CdHgTe thin-film Hall probes were used with 60Ω resistance each. The maximum current applied to feed the probes was less than 20mA, so that no significant power was dissipated.

In the case of mass spectrometers with permanent magnet, $B = \text{const.}$, and

$$m/e \sim 1/V, \quad (3)$$

where V is acceleration voltage of the ion beam, which is the highest potential in the ion source with respect to ground. Hence, to indicate the m/e ratio one has to reverse the high voltage (or its portion from a voltage divider). The reversed voltage can be displayed by means of the so-called double integrating digital voltmeter. Such voltmeters are commonly used in laboratories, DVMs with 4.5 digits are commercially available in panel version at price below 30\$. These voltmeters compare the measured voltage with a reference voltage produced by a specialized circuit inside the DVM. By reversing the inputs of “measured voltage” with “reference voltage” one can simply obtain the reversed voltage on the display. By adjustment of the voltage divider, a selected fraction of the high voltage is reversed in order to obtain the value of m/e ratio on the display.

4. CLEANING OF THE ION SOURCE

After the long-term work of the ion source the insulating ceramics and the lenses are covered by a semiconducting layer. The deposits are formed by the decomposition of the analyzed substances as well as by metal sputtered off the lenses by the high speed ions. This may produce quasi periodic breakdowns of the high voltage in the ion source or long-term instability of the ion beam due to permanent charging/discharging of the semiconducting layer on the surface of the ion lenses. During high voltage breakdowns the

ion currents can immediately disappear and appear soonafter. Such an erratic behavior of the mass spectrometer suggests that the ion source has to be cleaned.

The cleaning procedure described below is not difficult and can be done by the experienced operator. The ion source should be disassembled from the analyzing tube after venting the tube through a filter to avoid intrusion of any solid particles into the tube. The most dangerous are small ferromagnetic pieces which can be attracted by magnetic field of the analyzer. If the electromagnet is used then its power supply should be turned off during venting of the analyzer tube.

Having the ion source on the working table, whilst the hange of the analyzer diameter protected against dust by a piece of aluminum foil, one can disassemble the ionization cage and the lenses. Usually the ionization cage is the most dirty part of a gas ion source. It can be cleaned by removing the deposits by use of a delicate abrasive paper, e.g. 1/600 mm. The lenses can be cleaned in a similar manner. Use of distilled water for periodical rinsing of the parts is recommended. Finally, the parts are rinsed in acetone and cooked in distilled water. At this stage the lenses can be electropolished (see Peele and Brent 1977).

The electropolishing is a reverse electrolysis in a viscous strong electrolyte. It is a simple, effective and inexpensive technique. For electropolishing of stainless steel the following recipe for electrolyte can be used:

H ₂ SO ₄ (1.84 specific gravity)	1000 ml
water	370 ml
glycerin	1370 ml

Stirring, add the acid slowly to the water; avoid overheating. Cool to room temperature, then add the glycerin and stir well.

The electrolyte can be used for many cleaning procedures during which the cleaned part is immersed as a positive stainless steel electrode whilst a larger piece of steel foil surrounding that part is connected to the negative pole of a 24V/25A rectifier. The use of any other metals or alloys as nega-

tive pole is not recommended. The temperature of the electrolyte should be about 60°C.

The ceramic parts can be cleaned by abrasive paper, rinsed with distilled water, and finally boiled twice in distilled water. After thorough drying of all the parts in a clean furnace (at 70°C, overnight) the ion source can be assembled using clean tools only.

Ion sources of modern mass spectrometers have lenses which are mounted on sapphire balls for the best insulation and adjustment. This ensures long-term work of the source without cleaning and fast outgasing of the surface. In contrast, the outgasing of ceramic rods and wobbly ceramic spacers used in older ion sources is time consuming. Sparks due to trapped gas inside ceramic parts may appear when the high voltage supply is turned on too early. The tolerance of the sapphire balls can be as low as $\pm 3 \mu\text{m}$, which guarantees identical location of the lenses after cleaning or replacement.

5. STABILIZATION OF ELECTRON EMISSION CURRENT

Fluctuations of the electron emission current are immediately converted into fluctuations of the ion current. If one neglects the local pressure variations inside the ionization chamber, the variance of the ion current may be considered as linear combination of the variance of electron emission current and the variance of the ionization cross-section of gas molecules (this quantity varies with electron energy). Nowadays it is relatively easy to obtain the electron acceleration voltage (V_e) stabilized with the precision better than 0.01%. Hence, it is only the electron emission current (I_e) that may disturb the ion current stability.

There are two general types of electron emission regulators: series regulators and switching mode regulators. Regulators which utilize switching mode can offer several advantages over conventional, continuously controlled, series type regulators. In contrast to a well known series-pass regulator of filament current (Hałas and Sikora 1990) the comparator in the switching mode circuit has also a positive feedback loop formed by the re-

sistor connecting the noninverting input of operational amplifier (OA) with its output. This results in pulsation of the output voltage from -15V to +15V when the signal at the inverting input is slightly modulated around the reference voltage. Such a design leads to a self-oscillating stabilizer (Durakiewicz 1996). The simplified diagram of such stabilizer is shown in Figure 2.

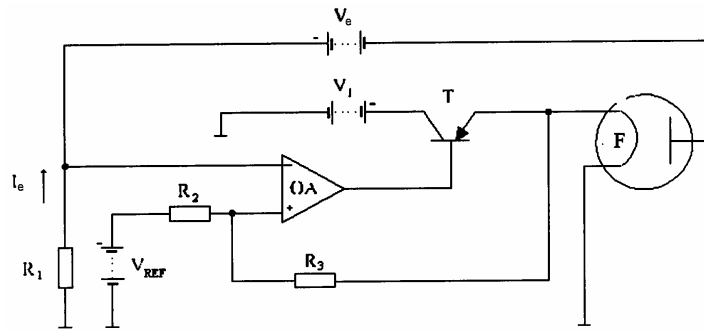


Fig. 2. Simplified diagram of the self-oscillating electron emission stabilizer. I_e is electron emission current, V_e is electron acceleration voltage, V_{REF} is reference voltage, and V_1 is filament supply voltage

Uproszczony schemat samooscyłującego stabilizatora emisji elektronowej

By applying the reference voltage to the noninverting input of the operational amplifier (OA) we force the transistor T to open. The value of the noninverting input voltage, V_{ON}^+ , is defined by elements R_2 and R_3 and voltages V_{ref} , V_1 and $V_{CE(SAT)}$, the latter being the saturation voltage of the opened transistor. V_{ON}^+ value is larger than V^- voltage being supplied to the inverting input of OA by the current-to-voltage converter, R_1 . V^- is equal to zero as long as no electrons are emitted from the filament. Hence, transistor T is opened, the filament, F, is heated and electron emission appears. As soon as V^- becomes equal to V_{ON}^+ the transistor is closed. The value of the voltage being supplied to the noninverting input varies depending on the state of transistor, being larger during heating of the filament. Therefore a certain amplitude of fluctuations occurs at the noninverting input, making the circuit self-oscillating. The frequency of the switching action depends on

V_{ref} , V_1 , $V_{CE(SAT)}$, R_1 , R_2 , R_3 and the filament time-constant (Durakiewicz 1996). Constant voltage is generated on the OA output in case of bad vacuum or any other break in the negative feedback loop. Use of capacitor (C_2 in Fig. 3) prevents the filament from being burned; such a protection may not be applied in conventional stabilizers.

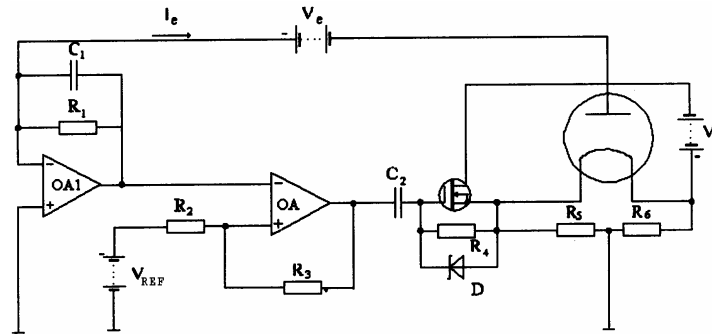


Fig. 3. A detailed schematic diagram of the self-oscillating electron emission controller. R_1 is 50k, R_2 is 10k, R_3 is 220k, R_4 is 100k, R_5 and R_6 are 100, C_1 is 10nF, C_2 is 47 μ F, D is C5V1, T is IRGPC50F, OA is μ A 741 and OA1 is CA3140

Szczegółowy schemat samooscyłującego stabilizatora emisji elektronowej

Although I_e is slightly modulated, its mean value remains extremely stable. Even after a few days of continuous work the mean I_e value did not vary more than 1%. The stability is not affected even by large variation of electron acceleration voltage from 40 to 100 V. The short-term instabilities of ion current induced by I_e modulation are negligible as long as the ion current detectors have the response time in the order of hundred milliseconds or larger. The long-term stability of the ion current is improved significantly, due to better stability of I_e . The mean I_e value is not influenced by the network supply voltage instabilities of amplitude 20%. A comparison of results obtained by electron emission stabilizers of various designs is given in Table 1. All the designs listed here except that by Durakiewicz (1996) are generally based on proportional regulation principle.

Table 1. Comparison of operation parameters of selected electron emission stabilizers
Porównanie parametrów wybranych stabilizatorów prądu emisji elektronowej

Ref.
Solution

	Chapman (1972)	Close & Yarwood (1972)	Herbert (1976)	Shaw & Lue (1980)	Hałas & Sikora (1990)	Durakiewicz (1996)
operation principle	proportional regulator	proportional regulator	proportional regulator	temperature stabilizer	double feedback proportional regulator	self-oscillating
stabilization coefficient	0.1%	0.1%	0.1%	>1%	1%	0.1%
relative cost	medium	low	very high	high	low	low
filament safety	–	–	safe start	–	safe start and loop break	loop break
I_e/U_e independency	–	–	+	–	–	+
energetic efficiency	<50%	<50%	<50%	<30%	<50%	<80%

The advantages of the pulsed heating for electron emission control may be summarized as follows : (i) low power consumption, the circuit may be used in a battery operated system (e.g. in satellites), (ii) self-protection against breaks in the negative feedback loop, including inner part of this loop between filament and electron collector (e.g. due to a bad vacuum), (iii) electron emission current is independent of the electron acceleration voltage and *vice-versa*, (iv) one pole of the electron acceleration voltage source is connected to the virtual ground of the system, thereby I_e does not influence the acceleration voltage itself, which property is important in mass-spectrometric study of the ionization phenomena by electron impact, (v) the circuit is simple and convenient in operation. The slight modulation of I_e with frequency above 100Hz by no means may be considered as a drawback in mass spectrometry and vacuummetry, where slow detecting devices for ion current measurements are used.

6. STABILIZATION OF FILAMENT TEMPERATURE

In thermal ionization mass spectrometry the ions are produced on the surface of a hot metal with high melting point (usually W, Ta, Re, Ir, Pt). The current density which can be drawn from the surface at equilibrium conditions is determined by the well-known Saha-Langmuir formula (Benninghoven et al. 1987, Valyi 1977):

$$j^+ = \frac{\nu}{1 + \frac{g^0}{g^+} \exp \frac{E_i - \phi}{kT}}, \quad (4)$$

where ν is the flux density of particles supplied to the surface, g^+ and g^0 are statistical weights of ground state of ion and neutral particle (for alkali metals the ratio g^+/g^0 is equal to 1/2), respectively, E_i is the ionization energy of the particle, ϕ is the work function of the metal, k is Boltzmann constant and T is the absolute temperature. The formula (4) is strictly valid only when the surface coverage is small.

For negative ions the respective formula is:

$$j^- = \frac{\nu}{1 + \frac{g^0}{g^-} \exp \frac{\phi - A}{kT}}, \quad (5)$$

where A is the electron affinity. Numerical values for electron affinities of some elements and their oxides can be found in Valyi (1977) and Wachsmann (1991, 1992).

Inasmuch as both nominator and denominator in formulae (4) and (5) are strongly temperature dependent, a precise filament temperature stabilization is required for production of stable ion beams by the surface ionization process. In the case of single filament ion source the flux density, ν , is driven by the surface diffusion from cooler ends of the filament towards its center. The filament center should be kept at a temperature at which the analyzed atoms can be effectively ionized, which means that the surface coverage is far

below the monolayer at the filament center. This condition is fulfilled for potassium at temperatures between 1000 and 1500K.

The design of the filament temperature stabilizer is based on the well proven idea of the Hałas-Kamiński bridge (Hałas and Kamiński 1995, Hałas et al. 1993, Durakiewicz and Hałas 1995). A conceptual diagram of the stabilizer is shown in Figure 4. The bridge contains a DC excitation voltage source, V_e . The excitation current passes through a diode and the bridge resistors but not through the transistor T. The R_F and R_V denotes, respectively, the resistance of the filament and a variable resistor used for temperature setting. The filament is made of pure metal like W, Ta, Re, Pt, which have positive and relatively large temperature coefficient of electrical resistivity.

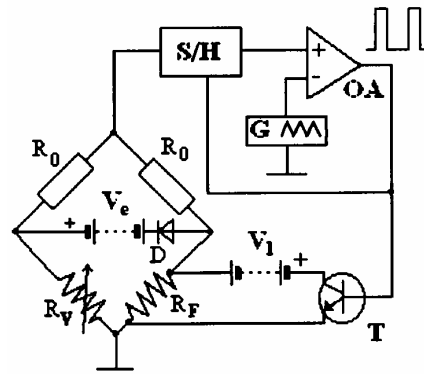


Fig. 4. Conceptual diagram of using the Hałas-Kamiński bridge for constant-resistance operation of a filament R_F . S/H is a sample-and-hold amplifier, G is a triangular wave generator

Uproszczony schemat układu z mostkiem Hałas-Kamińskiego do stałoprądowego grzania włókna metalowego

If $R_V < R_F$ then the bridge signal supplied to a noninverting sample-and-hold amplifier (S/H) is negative or zero and the transistor does not conduct. The noninverting input of OA is connected to the output of S/H amplifier while the inverting input of OA is fed by a positive signal from a triangular wave form generator, G. In the reverse situation, i.e. $R_V > R_F$ the imbalance signal generated by the bridge is positive and has a defined

magnitude. This signal is amplified by S/H which is holded at the output when the negative potential taken from the output of OA turns to positive. The comparator OA produces positive output voltage if generator signal is below the voltage holded by S/H. In this fraction of the cycle, transistor T conducts. Hence the power supply, V_1 , is connected in parallel to R_F (through T which plays a role of a switch). No significant current from V_1 can pass through the remaining parts of the bridge due to presence of the diode D. Because V_1 considerably exceeds V_e , the excitation current cannot pass through the low-resistance legs of the bridge (R_V and R_F) when R_F is supplied from V_1 . This is the reason for using a sample-and-hold amplifier instead of a normal operational amplifier.

As result of action of the circuit shown in Figure 4, the series of heating pulses is supplied to R_F with frequency driven by the generator but their duration is driven by the output voltage of the S/H amplifier. The bridge is always kept close to the balance state, i.e. $R_F = R_V$. If for some reason (e.g. voltage V_1 starts to diminish) R_F resistance becomes somewhat lower than R_V , then the bridge imbalance signal becomes somewhat higher, which results in longer duration of the heating pulses. A complete circuit diagram is shown in Figure 5. As the switching transistor a power MOSFET type IRGPCC50F was used. The gate of this transistor is protected by a diode C5V1. In selection of the power supplies, V_e and V_1 , a particular care on voltage stability was paid in the case of V_e . Commercially available switching regulators were applied (L4970) which are small-size and inexpensive.

The filament in our thermoemission ion source has two pairs of leads – one pair for V_1 power supply whilst the other for the bridge connection and high voltage supply. Those leads are connected to the four filament ports in the ion source flange. Potassium was loaded on a rhenium filament, $0.04\text{mm} \times 0.8\text{mm} \times 15\text{mm}$, as 25% KCl solution. After drying in air and degassing under vacuum, the filament was pre-heated in 800K. Ion emission was measured at filament temperature 1100K. Comparison of ^{39}K ion currents obtained by use of a MI-1305 mass spectrometer with solid-state ion source is shown in Figure 6.

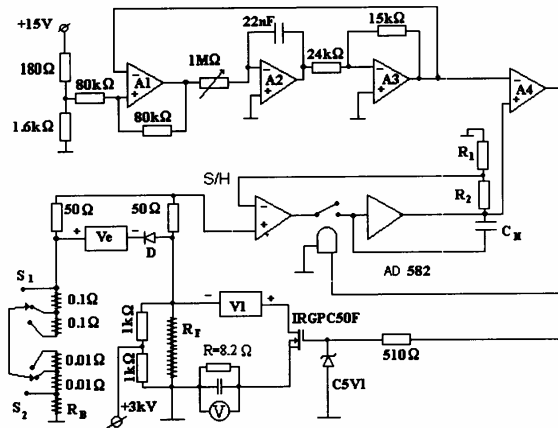


Fig. 5. Schematic diagram of filament temperature stabilizer. $A_1 - A_4$ are operational amplifiers comprised in LM321, $CH = 1\text{mF}$, $R_1 = 4\text{k}$, $R_2 = 800\text{k}$, V_e is a DC power supply (5V, 5A), V_1 is a DC power supply (10V, 5A). R_B is a two decades resistor made of manganin wire with total resistance of 1Ω

Uproszczonego schematu stabilizacji temperatury włókna metalowego

As it may be seen from Figure 6, the stabilization of filament temperature results in a lower variance of the measured ion currents, in comparison to filament voltage stabilization. The variance ratio is $V_V/V_R = 5.4$, where V_V is the variance of the ion current obtained with voltage stabilization, and V_R is variance of the ion current obtained with temperature stabilization.

The filament length is crucial in obtaining stable ion currents. A temperature *plateau* exists in case of long filaments. In such a case, the fluxes of ions are emitted from relatively large surface with fluctuations due to changes in surface coverage at the plateau region. Steady conditions for ionic emission were obtained only for relatively short filaments, for which no temperature plateau exists. Details on defining short and long filaments may be found in paper by Hałas and Durakiewicz (1998).

The electronic circuit presented in this section allows good temperature stabilization of a filament, by controlling the filament resistance. It was shown (Hałas and Durakiewicz 1998a) that filament resistance stabilization, being much simpler than the filament power stabilization, results in signifi-

cantly lower variance of the ion current than in the case of filament voltage or current stabilization.

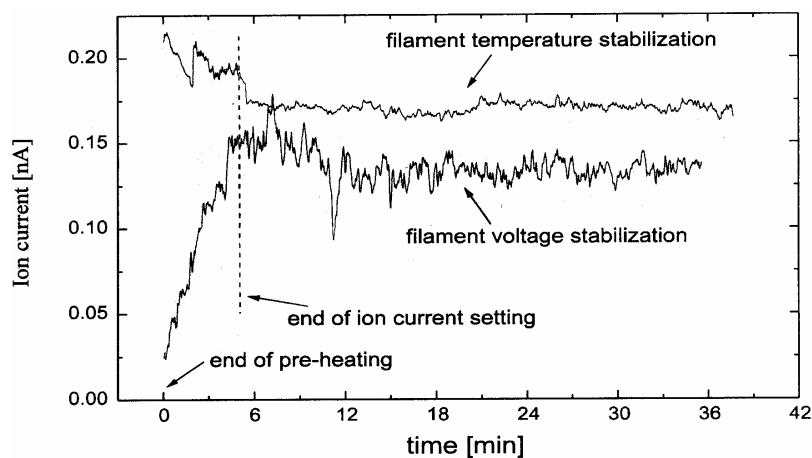


Fig.6. Comparison of ion ^{39}K currents obtained by the authors for filament temperature and filament voltage stabilizations
 Porównanie jonogramów (zapisów prądów jonowych) ^{39}K , otrzymanych przez Autorów w przypadku stabilizacji temperatury włókna oraz napięcia na zaciskach włókna

7. INTEGRATION OF THE ION CURRENTS

The ion detection system of a regular IRMS consists of the collector assembly containing two or more Faraday cups. Although the ion counting technique is used in specialized instruments for detection of very weak ion beams (like ^3He , ^{230}Th), it will not be discussed here.

The ions collected in each cup produce electric current which flows through a high-ohm resistor to the ground. The voltage produced on the resistor is not amplified but rather repeated by a circuit arranged as a voltage follower, or, more frequently, it is reversed by an amplifier with the resistor forming a negative feedback loop. A typical detector system of an IRMS is shown schematically in Figure 7. The ion current is converted to voltage by an operational amplifier with ultra-low input bias current and the high-ohm

resistor. The output voltages are then converted to trains of short pulses, the repetition rate of which is linearly proportional to the input voltage. These pulses are fed to separate counters which are set to zero at the start of measurement. When the major beam counter reaches a count of 10^6 , the minor beam counter is stopped and its value displayed. The value of the full six digit display is therefore equal to the current ratio.

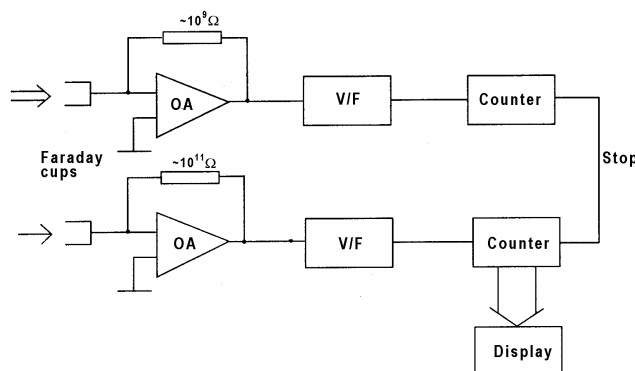


Fig.7. A typical arrangement for digital measurements of low current ratios. OA stands for operational amplifiers, while *V/F* for voltage-to-frequency converters
 Typowy układ do cyfrowego pomiaru stosunku prądów jonowych

The detection system described above introduces, however, its own noise to the results. This noise is generated predominantly by the high-ohm resistors. This is a fundamental phenomenon which cannot be totally eliminated by technological improvement of the production of high-ohm resistors (see e.g. Felgett and Usher 1980). Moreover, the resistors also suffer from fluctuations of their value due to variations of the potential drop along the resistor and temperature changes (Habfast 1960).

The key to improvement of isotope ratios measurement was to replace each high-ohm resistor, R , by a capacitor, C (Jackson and Young 1973, Hałas and Skorzyński 1980, McCord and Taylor 1986). The R to C replacement converts the ion detector from an ion “amplifier” to an “integrator” where the voltage on the capacitor raises in time proportionally to the charge collected

$$V = \frac{1}{C} \int_0^T I dt \approx \frac{I \cdot T}{C} \quad (6)$$

where C is the capacity, I is the ion current and T is the integration period. The capacity of the capacitor is selected in such a manner that the final voltages are in the order of 10 volts.

The integration period may be estimated from the following statistical considerations. Let us assume that the $^{18}\text{O}/^{16}\text{O}$ ratio is measured using CO_2 gas. Typical currents obtained by a Nier type ion source for mass 44 and 46 are $2.5 \cdot 10^{-9}\text{A}$ and $1 \cdot 10^{-11}\text{A}$, respectively. Hence, after time T the number of electrons collected on the capacitor is:

$$n \approx \frac{I \cdot T}{e} \quad (7)$$

where e is the elementary charge $1.602 \cdot 10^{-19}\text{As}$. According to the general statistical principles, the relative uncertainty of $\Delta n/n$ is equal $n^{-1/2}$, hence for the desired uncertainty of order of 10^{-5} the number of ions collected has to be 10^{10} . From equation (7) one obtains for the minor beam:

$$T \approx \frac{10^{10} \cdot 1.602 \cdot 10^{-19}\text{As}}{10^{-11}\text{A}} \approx 1.6 \cdot 10^2\text{s}. \quad (8)$$

The integration time has to be therefore of order of 100 seconds for a precision of the oxygen isotope ratios of 10^{-5} (0.01 permil).

The obvious inconveniences of the integrating system are that the capacitors have to be discharged periodically and the system cannot be directly used for the instrument adjustments. Both difficulties, however, can be easily overcome today by a computer controlled high quality reed switches for discharging the capacitors and their instant switching to the resistors. Such a solution was described by Hałas and Skorzyński (1980). One pair of reed switches is required for each amplifier. The switches are connected in parallel to C and R as shown in Figure 8. In the integrating mode the switch 2 is closed and switch 1 is used for periodical discharging of the capacitor.

For adjustment of MS, recording the mass spectra, etc., switch 1 is closed whilst switch 2 is open.

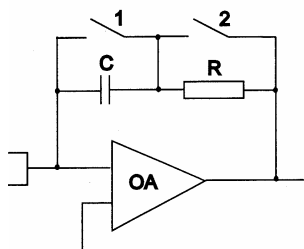


Fig.8. Schematic diagram of the capacitance/resistance system
Schemat układu pojemnościowo-opornościowego do pomiaru prądów jonowych

8. FINAL REMARKS

Good quality results are worth taking effort. The ideas and general remarks presented in this paper are certainly not the only solutions that guarantee success. They are, however, tested by many years of operation and maintenance of several IRMS's in our Mass Spectrometry Laboratory.

In the final section our reader should become aware that having the ion beams stable enough to produce satisfactory precision of 0.05 permil or better for standard *versus* standard does not guarantee identical precision for sample *versus* standard measurement. If this is not the case, one should check the purity of the sample and/or the gas flow conditions through the inlet system.

Having stable ion beams, pure samples and a high quality inlet system one has a chance for good and long-term performance provided that setting of the IRMS was favorable. The optimum setting of the ion source should assure maximum ion current at minimum electron beam. The gas flow rate through the capillaries should be selected depending on the geometry of the ion source. The pressure of the analyzed gas (as estimated on the basis of major beam current) during gas flow should not exceed significantly the

100-fold background pressure. Too high pressure leads to ion scattering on the gas molecules and thereby to peak broadening.

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STRESZCZENIE

W niniejszym artykule opisano praktyczne metody poprawiania stabilności prądów jonowych w spektrometrach mas, stosowanych do pomiaru stosunków izotopowych. Przedyskutowano kwestię niestabilności generowanych przez układ kolektora i źródło napięcia

antydynatronowego. Wykrywanie niestabilności pola magnetycznego następuje przy użyciu prostej konstrukcji wskaźnika m/e . Opisano również sprawdzone w praktyce metody czyszczenia źródła jonów. Ukazano rolę stabilizacji prądu emisji elektronowej w źródle jonów i przedstawiono autorskie rozwiązanie układu stabilizatora. Na koniec wykazano wyższość pomiarów prądów jonowych dokonanych przy użyciu integratora nad pomiarami uzyskanymi za pomocą wzmacniacza z oporem wysokoomowym.

