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Neon isotopic measurements using high-resolution, multicollector noble gas mass spectrometer: HELIX-MC

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[1] We describe a new high-resolution, multicollection, noble gas mass spectrometer, the HELIX-MC, developed by GV instruments. The instrument uses a collector housing that holds five "MiniDual" detection systems, each detector containing two devices: a Faraday cup collector and channel electron multiplier. Each detector is 5.2 mm wide, which permits collecting adjacent beams separated by 1 atomic mass unit (amu) at mass 136. The HELIX-MC operates at high mass resolution ($m/\Delta m > 1500$), which allows the interference of ⁴⁰Ar⁺⁺ on ²⁰Ne⁺ to be resolved. We report the results of some tests on the "MiniDual" collectors, in which we have achieved precise Ne abundance and isotopic measurements. After a correction for doubly ionized CO₂ (0.37–1.5%), our results show that the HELIX-MC produces only very limited instrumental Ne isotopic mass fractionation (\approx –0.5%.amu⁻¹). The sensitivity of the HELIX-MC for neon measurement performed on 10¹² ohms collector is around 1.4 × 10⁻³ A torr⁻¹ for quantities of ²⁰Ne analyzed comprised between 1.27 × 10⁻¹⁵ and 4.71 × 10⁻¹⁵ moles. Within this range, the reproducibility of the isotopic measurements of standard gas falls in the range between 0.5 and 0.8% (1 σ) for ²⁰Ne/²²Ne and 1 and 1.5% for ²¹Ne/²²Ne over a period of several days. The machine characteristics for measuring He are also reported.

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1. Introduction

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[2] Accurate determination of the isotopic composition of Ne in samples of geological interest poses several technological challenges. The most important are the isobaric interferences at m/z = 20 and 22 from ${}^{40}\text{Ar}^{++}$ and CO_2^{++} , respectively, which can induce considerable uncertainty in the measured ²⁰Ne/²²Ne ratio. Corrections are generally performed by measuring ${}^{40}\text{Ar}^+$ and CO_2^+ during the analysis with a subsequent correction at m/z = 20and 22, based on previously determined ${}^{40}\text{Ar}^{++/\!\!\!/40}\text{Ar}^+$ and $\text{CO}_2^{++}/\!\!\text{CO}_2^+$ ratios, respectively [e.g., Graf et al., 1994; Niedermann et al., 1997]. However, Nier-type ion sources commonly used in noble gas spectrometry are characterized by strongly pressure-dependent isotopic fractionation, on the order of several % per anu [Burnard and Farley, 2000]. In addition, as ${}^{40}Ar^{++/40}Ar^{+}$ and CO_2^{++}/CO_2^{+} ratios are also dependent on the spectrometer pressure at the time of measurement, it is impossible to totally deconvolve the m/z = 20 and 22 signals. This can be demonstrated considering the contributions to the various signals (S) at m/z = 20, 21 and 22 (assuming that the only contributions are the three isotopes of Ne, ${}^{40}Ar^{++}$ and CO_2^{++}):

$$\frac{S_{20}}{S_{22}} = \frac{{}^{20}Ne^+ + {}^{40}Ar^{++}}{{}^{22}Ne^+ + {}^{44}CO_2^{++}} = \frac{{}^{20}Ne^+ + \left({}^{40}Ar^+ \cdot R^{40^{++}/40^+}\right)}{{}^{22}Ne^+ + \left({}^{44}CO_2^{++} \cdot R^{44^{++}/44^+}\right)}$$
(1)

$$\frac{S_{21}}{S_{22}} = \frac{{}^{21}Ne^+}{{}^{22}Ne^+} + {}^{44}CO_2^{++} = \frac{{}^{21}Ne^+}{{}^{22}Ne^+} + \left({}^{44}CO_2^{++} \cdot R^{44^{++}/44^{+}}\right)$$
(2)

where $R^{40^{++}/40^+} = {}^{40}Ar^{++}/{}^{40}Ar^+$ and $R^{44^{++}/44^+} = {}^{44}CO_2^{++}/{}^{44}CO_2^+$ (independently known).

[3] If we express mass spectrometer discrimination, α , as a fraction per atomic mass unit:

$$\alpha_{\rm X} = \left[\left({}^{\rm i}{\rm X}/{}^{\rm j}{\rm X} \right)_{\rm measured} / \left({}^{\rm i}{\rm X}/{}^{\rm j}{\rm X} \right)_{\rm std} \right] / ({\rm i} - {\rm j}) \tag{3}$$

where i and j are isotopes of element X, then

$$\frac{S_{21}}{S_{22}} = \frac{{}^{21}Ne^+}{\alpha_{Ne} \cdot {}^{21}Ne^+ \cdot \left({}^{21}{}^{Ne} / {}^{22}{}^{Ne} \right)_{air} + \left({}^{44}CO_2^{++} \cdot R^{44^{++}/44^+} \right)}$$
(5)

Given that $R^{40^{++}/40^+}$, $R^{44^{++}/44^+}$ and α_{Ne} are all dependent on pressure, it is impossible to resolve the system because there are only two variables (the ratios S_{20}/S_{22} and S_{21}/S_{22}). Typically, users have ignored pressure-dependent instrumental fractionation, correcting only for the interferences.

[4] In order to target this problem, GV Instruments designed a new multicollector noble gas mass spectrometer, the HELIX-MC, with a sufficient mass resolution ($m/\Delta m > 1500$) to separate ${}^{40}\text{Ar}^{++}$ from ${}^{20}\text{Ne}^+$ (Figure 1). With this technological development, it is now possible for the first time to measure directly the instrumental Ne mass discrimination: resolving ${}^{40}\text{Ar}^{++}$ from ${}^{20}\text{Ne}^+$ removes one of the pressure-dependent variables from equations (4) and (5) ($\text{R}^{40^{++}/40^+}$), and consequently the system is tractable.

[5] A HELIX-MC instrument with five collectors was delivered to CRPG (Nancy) at the end of 2005. Here, we report the characteristics of this machine, its performance in terms of stability, reproducibility and discrimination, and its ability to achieve precise Ne isotopic measurements.

2. HELIX-MC Design

2.1. Mass Spectrometer Description

[6] The GV Instruments HELIX-MC is an all metal, 35 cm radius extended geometry, ultrahigh vacuum, noble gas mass spectrometer. The ionization of noble gases is achieved by electron bom-



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Figure 1. Scan across m/z = 20 at resolution $m/\Delta m = 1500$. In order to demonstrate that even large contributions of ${}^{40}\text{Ar}^{++}$ can be completely resolved from the ${}^{20}\text{Ne}^+$, the scan was performed without a liquid nitrogen cooled trap, increasing the ${}^{40}\text{Ar}^{++}$ signal by a factor $>10^3$ compared to the usual amount of Ar in the mass spectrometer during Ne analyses. The ${}^{40}\text{Ar}^{++}$ signal corresponds to 0.4 pA measured using a 10^{12} gain amplifier.

bardment in a Nier-type ion source. Ions are extracted from the source to the flight tube by a series of decreasing voltage focus-and-acceleration plates.

[7] The Nancy HELIX-MC has five "MiniDual" collector systems installed, each containing two measuring devices: a Faraday collector and channel

electron multiplier (hereafter EM, Figure 2). The axial "MiniDual" is fixed and provides a geometrical reference, while the remaining four collectors (Low 2, Low 1, High 1, High 2; e.g., Figure 3) are moveable via a series of micrometer screws, which enable multicollection of isotopes for all noble gases with exception of He, which can only be measured by magnetic peak jumping. Two of the five "MiniDuals" provide a high mass resolution $(m/\Delta m \approx 1500)$. The difference in mass resolution between the high-resolution collectors (L1, L2) and low-resolution collectors (Ax, H1, H2) is due to different focusing slits (0.3 and 0.6 mm respectively). The high-resolution capability of the machine compared to conventional noble gas machines is due to the larger radius of the flight tube (35 cm for HELIX-MC versus 27.5 cm for VG 5400, with the latter providing a mass resolution of only 600). It is also important to note that better voltage stability of the new generation HELIX-MC allows a higher mass resolution to be reached. Such a high mass resolution offers the possibility to completely resolve ${}^{40}\text{Ar}^{++}$ and ${}^{20}\text{Ne}^{+}$ (Figure 1).

2.2. "MiniDual" Description

[8] The "MiniDual" collector, shown in Figure 2, consists of a continuous dynode ("Channeltron") type electron multiplier (EM) mounted parallel to a Faraday cup with two dynodes that are used to deflect the beam between detection devices. An ion



Figure 2. Schematic drawing of the "MiniDual," containing two devices: a Faraday collector and a channel electron multiplier. (a) Ions beams pass through the entrance slit located before the entrance of the "MiniDual" and go straight to the Faraday collector when the dynodes are not turned on. (b) The ion beam is attracted on to the conversion dynode when a negative voltage is applied to the conversion dynode, which releases secondary electrons for each ion impact. Secondary electrons are then steered into the electron multiplier by applying a voltage to the intermediate dynode. Three suppression plates (two at ground, the closest to the cup at +150V) are found in front of the Faraday cup.

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Figure 3. (a) Schematic view of the collector housing. H2 collector is not shown. (b) Geometrical view of the different collectors used for Ne analysis and their position comparing to the axial "MiniDual" taken as reference. Collectors are moveable with micrometer screws along the y axis in order to achieve multicollection. Each detector is 5.2 mm wide, which permits collecting adjacent beams separated by 1 atomic mass unit (amu) at mass 136.

beam entering the collectors passes through the collector slit and will go straight through to the Faraday collector if there is no potential applied to the conversion dynode (Figure 2a). In contrast, if a negative voltage is applied to the conversion dynode, the ion beam is attracted to this plate, which releases secondary electrons for each ion impact (Figure 2b), which are steered into the EM by applying a potential to the intermediate dynode (Figure 2b).

[9] The standard Faraday amplifier resistors are 10^{11} ohm. However, there is an option with the HELIX-MC to fit Faraday amplifiers with 10^{12} ohm resistors, increasing the gain of small signals and improving Faraday/multiplier calibration. For Ne measurements, we installed a 10^{12} amplifier in the L2 position, allowing us to measure signals of 2×10^{-14} A of ²⁰Ne, resulting in better precision than would be obtained using an EM to count this isotope and enabling us to protect the sensitive channeltron multipliers from high beam intensities.

3. "MiniDual" Tuning

[10] Because of the geometry of the "MiniDual," there are potential sources of background noise on the electron multipliers, which influence the accurate determination of Ne abundances, especially ²¹Ne, the least abundant Ne isotope. We determined the electronic and "system" background noise, respectively, without ions reaching the EMs. The electronic background, generated within the EM and the pulse counting electronic compo-

nents (i.e., when the conversion and intermediate dynodes are turned off), is close to zero and is negligible for all the EMs. On the contrary, the "system" background, which corresponds to the secondary electrons emitted by the dynodes when their voltage is on, typically consisted of count rates of 0.5 to 1 cps but was highly sensitive to the dynode settings (particularly the conversion dynode voltage) and was variable between detectors: H2 for example had a "system" background as high as 4-5 cps and could not be used to measure low count rate isotopes; fortunately H2 was used for ²²Ne measurements which always represented beams of several hundred cps. ²¹Ne was measured in H1 (as opposed to the axial detector which would have been more logical) as the "system" background on H1 (0.1-0.15 cps) was lower than that of Ax (1-2 cps) and therefore produced better data for the low ²¹Ne count rates. All the Ne data presented here are corrected for the system background.

[11] As in conventional noble gas mass spectrometers, ion peaks with good mass resolutions and mass resolving powers are achieved by tuning the source parameters: repeller plate, trap currant, Y focus plates and (unique to the HELIX mass spectrometers) Z vertical plates. However, because of the beam deflecting dynodes of the "MiniDual" on the HELIX-MC, it is essential to optimize the peak shapes as a function of the voltage applied to the conversion and intermediate dynodes (Figure 4). For example, for the EM H1, a specific set of dynode voltages produce the best peak shapes for ²¹Ne. As shown in Figure 4, achievement of



Figure 4. Peak shape of ²¹Ne for different values of voltage apply on the intermediate dynode (from -15 to -75 V relative to ground). The conversion dynode is set at a voltage of -1100 V relative to ground. The maximum ²¹Ne signal here is ~ 2000 cps (such large ²¹Ne beams are only used only for tuning purposes).

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Figure 5. Signal of CO_2^+ versus CO_2^{++} measured at m/z = 22 and 44 in the mass spectrometer. The amount of CO_2 in the source is varied by progressively closing the titanium sponge getter.

optimum measurement conditions induces a small drop in beam intensity but this drop in signal is preferable given the gain in precision obtained by improving peak flat.

[12] The maximum possible multiplier efficiencies (where "multiplier efficiency" refers to the efficiency of the entire conversion dynode–intermediate dynode–channeltron multiplier system) varied from detector to detector and naturally depended on the dynode tuning; as stated above, dynodes were generally tuned to obtain good peak shapes rather than high sensitivity. Multiplier efficiencies were calibrated by initially measuring a stable (usually ²⁰Ne) beam of about 1×10^{-14} A on the Faraday cup and subsequently turning on the dynodes and measuring the same beam in the EM. Typical efficiencies were 45-55% relative to the Faraday collector.

4. Neon Standards

4.1. Conditions of Analysis

[13] Neon isotopes were analyzed following the procedure described by *Marty et al.* [1998], using an electron energy of 60 eV, but with a trap current of 400 μ A due to the analysis of He in the same samples. Gases were sequentially purified over two titanium sponges getters; one cycled between 600°C and room temperature, for 10 min, respectively, and the other was held at room temperature. Ar, Kr and Xe were cryogenically separated on an activated charcoal finger held at liquid nitrogen temperature for 15 min. Neon was adsorbed on a stainless steel grid cooled to ~30 K, leaving only

He in the purification line, which is introduced into the mass spectrometer for analysis. Following He analysis, Ne was desorbed from the cryogenic grid heated up at ≈ 60 K and was admitted to the HELIX-MC mass spectrometer. Before the analysis began, Ne was exposed for 5 min to new activated charcoal kept at 77 K in the source of the mass spectrometer in order to remove reactive gases background (notably CO₂ and hydrocarbons). The Ne isotopic composition was measured in multicollection mode with ²⁰Ne on the L2 Faraday collector, and ²¹Ne and ²²Ne on the EMs of H1 and H2 respectively (Figure 3b). The L2 Faraday collector was fitted with a 10^{12} ohm resistor, allowing a precise measurement of ²⁰Ne. Neon abundances and isotopic ratios were extrapolated to the time of introduction of the gas using in-house software. In order to obtain maximum reproducibility, we adopted the same time intervals for each step of the purification and analysis procedure. Typical analyses took approximately 30 min.

4.2. The ⁴⁰Ar⁺⁺ and CO₂⁺⁺ Corrections

[14] The major interference that affects the Ne isotopic composition determination is that of CO_2^{++} at m/z = 22. The mass spectrometer background was sufficiently clean that contributions from H₂¹⁸O and HF at m/z = 20 were ignored, and previous workers have shown that contributions by ²⁰NeH and ²¹NeH at m/z = 21 and 22, respectively, are negligible [*Niedermann et al.*, 1997] and, as stated above, ⁴⁰Ar⁺⁺ is resolved from ²⁰Ne⁺. As a consequence, it is not necessary to determine the ⁴⁰Ar^{++/40}Ar⁺ ratio to correct ²⁰Ne abundance.

[15] CO₂ is inherent to noble gas mass spectrometry because of degassing of the walls of the mass spectrometer from radiative heating by the filament. In addition, the valves produce a significant quantity of hydrocarbons that are broken down on contact with the filament to form CO₂. Contrary to the interference of ${}^{40}\text{Ar}^{++}$ on ${}^{20}\text{Ne}^{+}$, it is not possible to resolve ${}^{22}\text{Ne}^{+}$ and CO_{2}^{++} ($m/\Delta m \approx$ 6200 required). So, in order to correct the influence CO_2^{++} on the ²²Ne⁺ abundance, the double ionization ratio CO_2^{++}/CO_2^+ has to be determined. This ratio is sensitive to source tuning, therefore needs to be recalibrated each time any of the source parameters are changed. The mass spectrometer is put under static vacuum for 15 min to reach a measurable signal of background CO_2 on the EMs. The amount of CO_2^{++} in the machine was varied by progressively closing the titanium sponge getters.





Figure 6. Variability of the 20 Ne/ 22 Ne corrected for CO₂⁺⁺ contributions and a constant (non-pressuredependent) mass discrimination as a function of the amount of 22 Ne present in the source of the mass spectrometer.

 CO_2^+ was directly determined at m/z = 44 while CO_2^{++} was measured at m/z = 22 with the same source conditions as for Ne analysis. The amount of CO_2^{++} in the mass spectrometer is corrected from the contribution of ²²Ne by measuring ²⁰Ne, assuming then that Ne presents an air isotopic composition. It is interesting to note that when CO_2 amount reaches more than 50,000 cps, the CO_2^{++}/CO_2^+ ratio falls dramatically, probably as there are no longer enough electrons available in the source for multiple ionizations.

[16] The $R^{44^{++}/44^{+}}$ ratio, corresponding to $CO_2^{++}/$ CO₂⁺, determined for the HELIX-MC varied between 0.37 and 1.6% over a period of 6 months with several different source tuning parameters (Figure 5), which is consistent with the ratios determined in other laboratories on different kinds of noble gas mass spectrometer [Sarda et al., 1988; Hiyagon et al., 1992; Harrison et al., 1999; Aka et al., 2001; Moreira et al., 2001; Yokochi and Marty, 2004]. CO2 amount was measured for each standard performed on the HELIX-MC to correct its contribution on ²²Ne. Under typical running conditions, the CO₂ amount falls in the range between 3000 and 4000 cps, representing 5 to 10% of the m/z = 22 signal but varies by only a few % on a day to day basis. There was no discernable difference between the CO₂ signal when analyzing samples compared to standards.

4.3. Mass Discrimination and Reproducibility

[17] Mass discrimination is linked to a differential ionization yield as a function of the isotope con-

sidered. As a consequence, an ion beam produced and extracted from the source does not strictly reflect the isotopic composition of the gas present in the source of the mass spectrometer. In order to correct such distortion, the discrimination factor, D, has to be calculated for all Ne isotopes, as follows:

$$D = \left(\frac{\binom{i_{Ne}}{2^{2}_{Ne}}}{\binom{i_{Ne}}{2^{2}_{Ne}}}_{ref} - 1\right) * 100 \tag{6}$$

where std represent the value measured for the standard and ref the real value of this standard, given by Ozima and Podosek [2002]. We obtained a mean value of 9.69 and a mass discrimination of -0.5%.amu⁻¹ for ²⁰Ne/²²Ne, which is generally lower than the discrimination factors reported by other authors on different mass spectrometers (7.7%.amu⁻¹ [Marty, 1998]; 2.1%.amu⁻¹ [Pinti, 1993]; 1%.amu⁻¹ [Moreira et al., 2001]). It is important to note that the discrimination factor of the HELIX-MC did not vary much during a period of analysis of 10 days $(-0.5 < D < -1.5\%.amu^{-1})$, although it should be emphasized that these discriminations were calculated assuming that there was no pressure dependence on the ${}^{40}\text{Ar}^{++}/{}^{40}\text{Ar}^{+}$ and CO_2^{++}/CO_2^+ ratios. As reported by *Burnard and* Farley [2000], noble gas ion sources can induce strong pressure dependence on the discrimination of the noble gas isotopic ratios. In order to correct a potential bias of the Ne isotopic determination by the HELIX-MC, we performed standards with different Ne partial pressures, varying from 1.5 \times 10^{-16} to 6×10^{-16} moles of ²²Ne (Figure 6). The results obtained show there is little or no variation within the error bars of the Ne isotopic measurements as a function of 22 Ne abundance in the source (Figure 6). Therefore, under these source conditions, there is no need to apply a pressuredependent mass discrimination to Ne isotopic measurements.

[18] The reproducibility for the Ne isotopic composition of a set of ≈ 25 standards of between 1.27×10^{-15} and 4.71×10^{-15} moles, covering periods of 5-10 days, are between 0.5 and 0.8% for 20 Ne/ 22 Ne and between 1 and 1.5% for 21 Ne/ 22 Ne (1 σ). The sensitivity of the HELIX-MC is around of 1.4 $\times 10^{-3}$ A torr⁻¹ for neon measurements. During a single day, it was possible to reach a precision of 0.1% on the 20 Ne/ 22 Ne ratio of 10 consecutive standards. However, this experiment only serves to test the instrument, because analysis of 10 standards does not allow any actual samples to be



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Figure 7. Variability of the ${}^{3}\text{He}/{}^{4}\text{He}$ as a function of ${}^{4}\text{He}$ present in the source of the mass spectrometer. ${}^{3}\text{He}/{}^{4}\text{He}$ of the standards are normalized to the one with the higher He quantity (taken as reference).

analyzed within the same day. The main reason for the observed uncertainties was the instability of the dynodes and the progressive decrease in the efficiency of the H1 EM which reduced by about 1% over this time scale. Indeed, because of this deterioration, we had to retune the dynodes' values and the EM voltage every 10-15 days. Such instability strongly influences the reproducibility of the measurements. Uncertainties also come from the fact that the performance of the 15-year-old purification line used in this study cannot match that of a modern, fully automated gas delivery system.

[19] The most important problem to be addressed for future analyses is to achieve a better stability of the EMs' yields, as it would greatly improve the precision on the ²¹Ne/²²Ne ratio. Nevertheless, the reproducibility reported here for standards with low amount of Ne (e.g., 1×10^{-15} moles of ²⁰Ne) could be used to determine the Ne isotopic composition for rocks, as mid-oceanic basalts, with excellent precision.

4.4. Helium Isotope Measurements

[20] Although the HELIX-MC is not optimized for He isotope measurements, it is possible to measure these by changing magnetic field and alternately measuring ⁴He (in a Faraday Cup) and ³He (with an EM). In general, there is no significant advantage measuring He isotopes with a 10^{12} gain amplifier given the large ³He/⁴He ratio in terrestrial samples. Also, it would be counterproductive to measure He beams using high-resolution detectors because the He peak is considerably narrower, in terms of magnetic field, than heavy noble gas peaks and magnetic field stability could be an issue. Consequently, ⁴He is measured using H2

FC (resolution \sim 700 m/ Δ m) and ³He using H1 EM (the MiniDual with the least noise; resolution \sim 700 m/ Δ m).

[21] With a filament current of 400 μ A and all other source parameters optimized for He (essentially this involved changing increasing the electron volts for He measurements to ~75 eV and adjusting the beam focus), the machine sensitivity for ⁴He was 1.7 × 10⁻⁴ A torr⁻¹ comparable to other mass spectrometers with Nier-type sources (VG5400, MAP215), but was largely linear within the pressure range investigated (Figure 7; P⁴He ~ 2×10^{-10} – 2×10^{-8} mbar, corresponding to signals between 6×10^{-14} and 6×10^{-12} A ⁴He). However, in common with other Nier-type sources [*Burnard and Farley*, 2000], the ³He/⁴He discrimination of the mass spectrometer is a function of He partial pressures in the mass spectrometer, reducing by ~5% at low He partial pressure.

5. Conclusion

[22] GV instruments recently delivered to CRPG (Nancy) a high-resolution, multicollection, noble gas mass spectrometer with five "MiniDual" collector systems, each containing two devices: a Faraday collector and channel electron multiplier. The HELIX-MC produces a mass resolution $(m/\Delta m)$ of 1500, which allows the interference of 40 Ar⁺⁺ on 20 Ne⁺ to be resolved. The ratio CO₂⁺⁺/CO₂⁺ for this instrument was found to be in the range 0.35–1.5% and allows for a correction of the interference of doubly charged CO₂ on 22 Ne⁺. Furthermore, the HELIX-MC does not produce significant mass discrimination among the Ne isotopes, and the reproducibility of standards (1 σ) falls between 0.5 and 0.8% for 20 Ne/²²Ne and between 1 and 1.5% for 21 Ne/²²Ne for 30 consecutive analyses over 10 days.

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