water from $m/z$ 230 produces the ion at $m/z$ 212. A wider mass range daughter spectrum ($m/z$ 90–290) shows an abundant peak at $m/z$ 133, characteristic of peptide bond cleavage to yield a (Gly-Gly + H)$^+$ fragment. The daughter spectrum of the protonated tripeptide Gly-Gly-Gly also yields an abundant ion with $m/z$ 133. The base peak in the daughter spectrum of (Gly-Gly-Gly + H)$^+$ is 115$^+$, due to loss of water from $m/z$ 133.

The LDCI mass spectral data for the amino acid arginine (free base) are included in Table I. Collision-induced dissociation of protonated arginine, $m/z$ 175, yields an even more characteristic spectrum including the ions $m/z$ 175 (100%), 158 (15%), 130 (50%), 116 (80%), and 112 (25%). The fragment ion 158$^+$ results from ammonia loss from the guanidyl group (*23*). Formation of the daughter ion $m/z$ 130 results from the loss of $NH_3$ and CO from the parent ion (*23*). The ion at $m/z$ 116 can be rationalized by loss of HNC(N-$H_2$)$NH_2$ from the amino end of the molecule. The fragment ion $m/z$ 112 can result from loss of ammonia and formic acid from $m/z$ 175.

## CONCLUSIONS

The disadvantage of the present method is the use of a scanning mass analyzer with a pulsed method of ionization, resulting in inefficient use of sample. The advantages of implementing the device include its adaptability to any system with a vacuum interlock. The fiber-optic probe has proven to be extremely rugged and has provided reliable operation over a period of months. In addition, the use of this device in the triple quadrupole mass spectrometer with its on-axis detector resulted in a significant reduction of spurious detector noise (neutrals or photons) compared to an orthogonal arrangement of the laser beam and solids probe.

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# High-Precision Conductivity Measurement Bridge with Variable Frequency

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Conductivity measurements are most suitable for evaluating phenomena such as interionic forces (*1*) and ion association (*2*). Furthermore chemical reactions can be monitored which lead to changes in the ion concentration (*3*). Precise conductivity measurements, however, can only be performed by varying the frequency since the impedance of the electrode double layer is only negligible compared to the impedance of the electrolyte at sufficiently high frequencies. At the same time the frequencies chosen should not exceed an upper limit depending on the actual solution in order to achieve highest sensitivity. A frequency range from 200 Hz to 20 kHz is most suitable to cover a large concentration range for any electrolyte.

Any ac oscillator produces, in addition to the fundamental frequency, minor amounts of harmonics. Since an ac bridge can only be balanced for a distinct frequency, these overtones reduce the sensitivity.

This problem can be solved by applying a band-pass filter which is tuned to the fundamental. Either some distinct oscillator frequencies with suitable fixed filters can be used or a tunable filter has to be applied if the frequency is to be continuously varied. In the first case the procedure is limited to only a few frequencies and the second proves to be rather cumbersome.

These difficulties can be elegantly overcome by the use of modern switched capacitor filter circuits.

Any standard filter function can be configured with this type of integrated circuit by a simple resistor network, which independently adjusts the filter parameters such as filter quality and gain. Additionally, a sine-wave oscillator can be realized in this manner. One external clock, necessary for the operation of these integrated circuits, exclusively determines the characteristic frequencies of both oscillator and band-pass filter in the same manner. Multistage filters are easly established since up to four second-order filters are integrated in one package.

## EXPERIMENTAL SECTION

For the construction of both the sine-wave oscillator and the band-pass filter of eighth order, switched capacitor devices (e.g., R5621 or R5622, respectively, from Reticon, Sunnyvale, CA) were used. The block diagram can be seen in Figure 1. A free running multivibrator (C) was used for generating the clock frequency (50% duty cycle square wave). The output of the sine oscillator (O) is connected to a push–pull power amplifier (P), followed by

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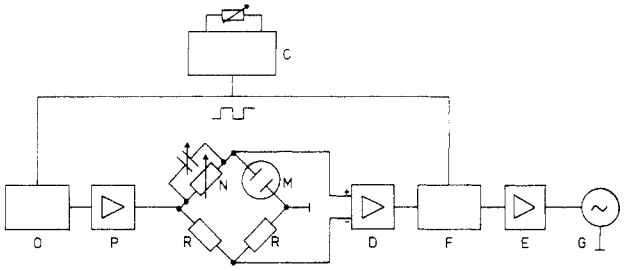


**Figure 1.** Block diagram of the bridge for measurement of electrolyte conductivity.

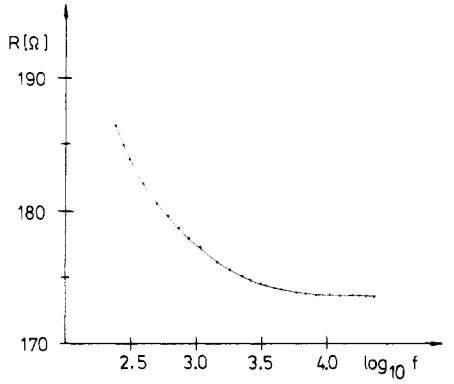


**Figure 2.** Frequency dependence of the resistances of an aqueous 0.1 M KCl solution at 25 °C for the determination of the cell constant. For this low resistance the precision is confined to ±0.1 Ω due to the resolution of the resistor decade. The limiting value of the resistances for high frequencies yields the cell constant of 2.232 ± 0.001 $cm^{-1}$ (0.012 856 $\Omega^{-1}$ $cm^{-1}$ specific conductivity for the 0.1 M KCl standard solution (*5*)).

a Wheatstone bridge arrangement (conductivity cell (M), precision resistor decade (N) type 1407 0–1.1 MΩ 0.02% accuracy in steps of 0.1 Ω (Burster Messgerätetechnik, Gernsbach, Germany), and high-precision wire resistors (R) 2 × 1 kΩ 0.005%).

The bridge voltage is fed to a differential preamplifier (D). The overtones are canceled by the switched band-pass (F), which is supplied with the same clock frequency as the sine oscillator. The balance of the bridge can be observed after amplification (E) with an oscilloscope.

Circuit diagrams are available on request.

## RESULTS AND DISCUSSION

The available frequency range of the conductivity bridge can be varied from 250 Hz to 20 kHz. According to Figure 2 the solution resistances have to be extrapolated to high frequencies to determine the cell constant (*4*). An extreme example was chosen (0.1 M KCl at 25 °C (*5*)), which leads to a low resistance near 170 Ω for the electrode used and therefore an appreciable frequency dependence is observed. These conditions can be realized since the sine oscillator delivers a high output current (about 300 mA). Usually the resistance of the investigated solution, however, should be within the range of 300 Ω to 30 kΩ to benefit from the whole accuracy of the resistor decade without problems from capacities.

The intensity of the first harmonic wave is diminished by more than 98% in the whole frequency range. Therefore the bridge can be balanced with a sensitivity better than 0.005% in the resistance range of several kiloohms. The accuracy of the whole arrangement is therefore not limited by the bridge balance but mainly by the precision of the resistor decade (in this case 0.02%) and the temperature control of the electrolyte solution.

A modulation of the output voltage in the magnitude of 30 mV, due to the specific design of a switched capacitor filter, can be canceled easily by a simple active second-order low pass, because the clock frequency differs from that of the sine wave frequency by a factor of 25.

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