Element Analysis Without Standards in Spark Source Mass Spectrometry with Low Voltage Vacuum Arc Discharge and Automatic Photoplate Evaluation

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Summary. With a system for automatic evaluation of photographic plates in spark source mass spectrometry, the complete information on the photographic plate is used for the concentration procedure, i.e. all isotopes of singly and multiply charged ions contribute to the analytical results. Experiments show that the ion intensities of elements in their various ionization states lie on parabolas. The position of the parabola of impurity elements within a matrix depends mainly on that matrix and shows a characteristic relation to the analytical result.

Systematic investigations lead to a significant parameter, the "mean charge number" $Z_m$, which forms a common link between the very different parabola positions of all elements within a matrix. This knowledge is the basis of a new evaluation procedure which, without using a calibration standard, leads to an essential improvement of the analytical result. Experiments in practical analysis in the analytical service of the central department demonstrate that this method, applied to many different matrices, shows a maximum deviation from the certificate value by a factor of 2 (in many cases <1.5).

Determinations of the major components of alloys yield accuracies between 10 and 20% (deviations of the analytical result from the certificate value). For the relative standard deviation of the analysis results an upper limit of 15% was reached.

Key words: Elementanalyse; Massenspektrometrie, Funken; leitprobenfrei, automatische Photoplattenauswertung

1. Introduction

In the preceding series of papers the significant advantages of spark source mass spectrometry are outlined more than once: almost all elements can be detected simultaneously within a single analytical operation, with low detection limits, and with almost negligible...
expense for sample preparation. A basic disadvantage is the frequently insufficient accuracy [13, 14] of the method. The performance of spark source mass spectrometry has been described by Morrison and Skogerboe [12]. Improvements are achieved by using calibration standards to evaluate "relative sensitivity factors" (RSF) [10]. The typical range of these calibration factors is 0.2 to 5 [1, 11].

In practical analysis, there is a decisive reason to avoid the calibration method, because for more than 90% of typical problems in spark source mass spectrometry, suitable standards are missing. In most cases, the standards offered by manufacturers are only alloys of technical interest. Owing to the high requirements upon homogeneity, it is hardly possible to produce own standards for multielement analysis. Many attempts have been made to develop spark source mass spectrometry to a stage that permits analyses without reference samples. With regard to the insufficient understanding of the process of ion formation this aim has not been reached until now. The present study is not an attempt to enlarge the theoretical knowledge of the process of ion formation, but rather aims at establishing systematic trends derived from an abundance of analytical data, which were obtained by means of an existing evaluation facility [8, 15]. Therefore a substantial reduction of analytical errors was possible.

2. Experimental Conditions

2.1 Mass Spectrometer

The mass spectrometer available at Central Department for Chemical Analysis at KFA is a double focusing Mattauch-Herzog type with triggered low voltage d.c. vacuum arc discharge (abbreviated as "vacuum arc") and photoplate detection (SM1-B/F, Varian MAT, Bremen). It has proved to work expediently with a resolving power (M/ΔM) at a 10% valley-point of about 1,000–1,500.

In view of the objectives mentioned above, the use of a vacuum arc discharge as an ion source is of particular significance [3, 19]. Compared with the normally applied radio frequency (RF) spark discharge, the vacuum arc has the following significant differences [4, 6, 7, 9, 22]:

- The energy distribution of the ions emitted from the vacuum arc is by one order of magnitude lower than that of the ions from the RF spark. This applies only to that stage of the arc discharge that follows after the ignition phase. The ion current originating from this arc phase is faded ion-optically at adequate intervals and utilized for analysis [20]. Owing to the small energy range of the ions, the mass lines on the photographic plate exhibit a rectangular profile with line width independent of blackening [6, 7, 9]. This makes it possible to use the plateau value of line blackening instead of the integral of the line profile as a measure for intensity. It is further possible to detect even partially overlapping lines by their rectangular superposition profile.

- The vacuum arc furnishes a periodic sequence of steady state single discharges with constant current [6, 7, 9], i.e. the time average of one discharge phase also represents the instantaneous state (RF: transient). Until a few years ago the general opinion prevailed that the vacuum arc discharge involves a plasma in local thermal equilibrium (LTE) [3, 19]. In 1974, Stüwer [20] succeeded in proving experimentally that this assumption was erroneous.

- Besides singly charged ions, the low-voltage arc discharge in vacuum also furnishes ions of higher ionization states. For quite a number of elements, the twofold or threefold ionized state is even more frequent than the single charge condition. In contrast to this, RF spark discharge furnishes primarily singly charged ions.

- The ratio of multiply charged to singly charged ions is constant in time. This very important property of the vacuum arc basically permits the use of all types of ions for analysis.

2.2 Evaluation Instrument

The unit for automatic evaluation of photographic plates consists of a spectrum plate comparator (Leitz-MAT Comparator PAM 2) connected with a computer system 620/L Varian MAT, Bremen. Scanning of the plate (Ilford Q2) is effected at a constant velocity of 5 mm s\(^{-1}\) in the longitudinal direction of the plate. This system permits transmittance measurements on the plate at constant intervals of 2 μm with continuous motion of the carriage. In this way, the mass lines of all elements of the unknown sample can be detected and used for analysis. This is an essential characteristic of a progressive method for multielement analysis [23].

The effective slit width of the scanning system is 5 μm. In connection with the path increment of 2 μm used, several transmittance measurements are thus guaranteed within line plateaus of even the smallest line widths (15 μm at the light mass end).

The carriage velocity (5 mm s\(^{-1}\)) and the path increment for transmittance measurements (2 μm) give a transmission rate of 2.5 kHz for measured values into the connected computer where these data are further processed by the program system. The computer has a core memory capacity of 24k words with a word length of 16 bits each. The cycle time is 1.8 μs. Connected to this system are the following external devices: a cartridge disk, a digital plotter, a high-speed printer, a card reader, and a console typewriter.

3. Evaluation Method for Quantitative Analysis without Standards

3.1 Overview

The procedure for the automatic evaluation of photographic plates consists of two steps:

An "on-line" step comprises data acquisition, data reduction, and correlation of measured values, and an