Separation of analytical signal for atomic-emission microwave plasma measurements

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Abstract. The analytical signal for atomic-emission microwave plasma (AEMP) spectral analysis method is studied. It is shown that the signal consists of two parts: background signal, proportional to content of the analytical element in a sample shaped by submicron particles and metalorganic compounds; pulse signal, proportional to content of analytical element in coarse discrete particles. The “dynamic discrimination” algorithm is suggested that allows measuring the element content in a liquid or powder ore sample independently of the content shape using AEMP method. It is shown that atomic absorption (AA) and AEMP measurements of Fe, Cu agree within error for samples both low and high in content of element in submicron particles.

1. Introduction

Atomic-emission microwave plasma (AEMP) [1] spectral analysis method, also called scintillation method, is based on continuous introduction of the sample into the spectrum excitation source. The sample usually consists of powder of discrete particles [2]. The atomized sample matter produces light flashes (scintillations), which are registered as pulses by the equipment. The equipment counts pulses that have amplitudes exceeding specified threshold. Thus, equipment noise is not registered. This approach to signal extraction was developed by researchers during almost 40 years for precious metals analysis in powder ores [3-5]. The main task was to develop a method to express measurement of parameters of precious metal content. In particular, mass fraction, fineness and particle size of gold was measured.

The task was solved partially. The matter is that metallic impurity can take shape of uniformly dissolved (metalorganic) particles with size so small, that produced pulses do not exceed equipment noise level. The work [6] shows that this impurity consists of particles below 2 um in diameter (submicron particles). Inability to account for submicron impurity results that method lies in category of semi-quantative analysis.

Liquid samples are analysed using atomizer (sprayer) for sample introduction [7]. Oil samples and filter wash samples of aircraft engine systems are analysed for tribodiagnostical purposes [8]. In these samples, mass fraction of submicron particles can exceed 50 %. Therefore, the precision of method can be increased significantly by accounting for submicron impurity in a sample.

For AEMP measurements so called “scintillation principle” is defined. The principle is usually formulated as such – the probability of simultaneous presence of multiple discrete particles in analytical field of spectrum excitation source must be minimal, i.e. particles must reach the plasma one
by one. In other words, adherence to the principle enables the ability to register the signal from each particle individually.

In real samples, particles are distributed lognormally and most common case is that the signals from multiple submicron particles overlap over each other and “scintillation principle” is violated. The edge case is registering uniformly distributed impurity, i.e., when metal is present in sample in shape of true solution (metalorganic compounds). In these conditions each solid particle for powder ore samples or each drop of liquid sample can be viewed as separate “portion” that contains analytical element. As these “portions” are introduced to spectrum excitation source, the background signal value increases and coarse particles will produce significant pulses on the increased background.

This paper aims to develop mathematical description for separate extraction of analytical signal for both submicron elemental impurity and impurity in coarse discrete particles; develop corresponding software and perform experimental verification of the developed method for signal extraction.

2. Analytical signal for uniformly distributed impurity

Let the sample introduction device generate N “portions” in a time unit. A number of similar pulses with different amplitude but same shape forms the analytical signal in this case. The time of a pulse beginning is an evenly distributed random variable. The expression for the signal can be written as

\[ S(t) = \sum_{i=0}^{\infty} a_i v(t - t_i) \]  

where \( a_i \) – pulse amplitude (depends on the size of the “portion”), \( v \) – pulse shape (same for every “portion”), \( t_i \) – the sequence of random time moments of pulse beginning (Poisson point process with mean rate \( N \)). Since the pulses overlap continuously, this process can be approximately described as a Gaussian process with characteristics

\[ M\left[ S_u(t) \right] = N M\left[ a_i \right] \int_{-\infty}^{\infty} v(t)dt \]  

\[ D\left[ S_u(t) \right] = N M\left[ a_i \right] \int_{-\infty}^{\infty} v^2(t)dt - M^2\left[ S_u(t) \right] \]  

where \( M[S_u(t)] \) – the mean signal value, \( D[S_u(t)] \) – variance.

As such, the mean signal value does not depend on time in this case and is proportional to the amount of generated “portions” and quantity of metal within. The variance also does not depend on time and increases with mean amplitude \( (M[a_i]) \) which is proportional to “portion” size.

Since Gaussian random process is ergodic, using (2) we have

\[ \bar{S}_u = \frac{1}{T_e} \int_0^{T_e} S_u(t)dt = M[S_u(t)] \propto N \cdot \bar{m} \propto C_u \]  

where \( \bar{S}_u \) – mean signal value through exposition,
\( \bar{m} \) – mean particle mass in a “portion”,
\( C_u \) – mass fraction of uniformly distributed impurity.

Therefore, mean value of analytical signal through exposition is proportional to content of uniformly distributed impurity and the variance of analytical signal decreases with “portion” size.

3. Analytical signal for discrete impurity

Now we will consider the case where the probability of simultaneous appearance of two or more particles in spectrum excitation source is approaching zero. As such, there will be periods of time when either one pulse is present or there are none (the signal is zero). The area of each pulse will contain information about evaporated mass. The expression the for signal is
where \( n \) – amount of particles in sample, \( I_k(t) \) – \( k \)-th particle pulse.

Most common case in real situation is some intermediate scenario, when signals from submicron particles (present in large quantity in the sample) will overlap and cause the increase of a background signal, indistinguishable from increase, caused by dissolved, uniformly distributed impurity. The coarse discrete particles will produce significant pulses on this background.

The general case for expression (1) can be formulated as follows:

\[
S_i(t) = \sum_{i=1}^{n} a_i(t - t_i) + \sum_{k=0}^{n} I_k(t) + S_p(t)
\]  

(6)

The first addend describes the signal constituent, shaped by uniformly distributed and submicron impurity. The second – the constituent, caused by discrete impurity, and the third – the noise constituent. The latter is caused by equipment noise, which raises the background signal has its own mean and variance.

The task now is to discriminate significant pulses from noise background. This can be accomplished using different approaches, most trivial being the “thresholding” approach. The second constituent in expression (5) can be written as

\[
S_i(t) = \sum_{k=0}^{n} I_k(t) + \sum_{j=0}^{n} I_j(t)
\]  

(7)

where first addend is the totality of small overlapping pulses, and second is totality of separate non-overlapping pulses. Finally, the analytical signal expression can be written as sum of gaussian and pulse random processes:

\[
S(t) = S_G(t) + S_i(t)
\]  

(8)

Gaussian random process is shaped by three constituents: noise background signal (plasma and equipment noise), signal from uniformly distributed impurity and signal from submicron particles

\[
S_G(t) = S_N(t) + \sum_{i=1}^{n} a_i(t - t_i) + \sum_{k=0}^{n} I_k(t)
\]  

(9)

Mean exposition value of this signal is given by

\[
\bar{S}_G = \frac{1}{T} \int_{0}^{T} S_G(t)dt = a_N + b \cdot C_U + c \cdot C_M
\]  

(10)

where \( b, c \) – proportion coefficients, \( C_U \) – mass fraction of uniformly distributed impurity, \( C_M \) – mass fraction in submicron particles.

The second addend in expression (7) describes the signal from random pulse process, discriminating which is the main task of AEMP measurements:

\[
S_p(t) = \sum_{k=0}^{n} I_k(t)
\]  

(11)

The mean value of this signal is proportional to mass fraction of element in discrete particles \( C_D \):
\[ \overline{S}_D = \frac{1}{T_D} \int_0^T S_D(t) dt \propto C_D \]  

(12)

We will note some extra factors that affect the characteristics of analytical signal:
1. Unstable output of the liquid sprayer (mean quantity or size of the drops can differ over time);
2. Parameter fluctuations of spectrum excitation source.

Due to these factors background signal value can slowly change over time. Formally this is equivalent to a pulse with small amplitude and high duration. This part must be excluded from pulse signal.

4. “Dynamic discrimination” algorithm

As it is shown above, the analytical signal in general case is constituted from two random signals:
1. Continuous signal with small noise amplitudes, slow change of the mean over time, which is proportional to the mass fraction of dissolved element and element in submicron particles;
2. Pulse signal – separate non-overlapping pulses with big amplitude, proportional to mass fraction of element in coarse particles.

The figure 1 shows pulse signals (signal intensity over time) overlapped with continuous, slowly changing signal (a) and the picture for signal parts after their extraction, that must be achieved (b, c).

![Figure 1. Overlapping background and pulse signals.](image)

The simplest way for this is a software one. The algorithm for “dynamic discrimination” (Figure 2) works as follows. The overall signal is smoothed out as moving average of 5 samples. The registration begins in “background” mode. Every signal sample is treated as a background one – that is, proportional to mass fraction of submicron impurity. The plasma constituent of the background signal is written at the start of the exposition and is corrected for later. When the signal rate of change exceeds the specified value \( L_D \), the “particle” registration mode begins and signal value at the time is remembered as “background” threshold. The value \( L_D \) is called “discrimination level”. In “particle” mode, the signal above the “background” threshold is treated as proportional to the mass fraction of coarse particles.

The pulses are additionally discriminated by duration. The pulses durations are dependent on the temperature distribution of spectrum excitation source and the time which impurity spends in
analytical (high temperature) zone. The durations vary from hundreds of us [3] to 1’s of ms [9]. The spectrum excitation source for AEMP measurements [6] allows full evaporation of particles up to 60 μm in size in 1-10 ms. This makes the discrimination by duration an easy task – 1-10 ms thresholds are used for signals in “particle” mode.

The “discrimination level” is set in such way that sample that does not contain coarse particles and does not produce a single pulse. As this sample, the “Conostan” type sample is used, for which elements are introduced to the oil in the form of metalorganic complex.

Using the “dynamic discrimination” approach, registered “particle” mode signal is shown on the fig. 1, c. The “background” mode signal – on fig. 1, b. I.e., required signal separation was achieved.

![Flowchart](figure2.png)

**Figure 2.** Flowchart for “dynamic discrimination” algorithm, 
- $S(t_n)$ – signal in time moments $t_n$;  
- $B$ – background signal value (output);  
- $I$ – pulse signal value (output);  
- $M$ – background signal threshold;  
- $L_D$ – “discrimination level”.

The signal separation results in two analytical parameters – mean background (expression 10) and pulse (expression 12) signal values throughout exposition. The mass fractions in these expressions can be determined after proportion coefficients are found via equipment attunement, i.e. measuring standard samples with known content.

**5. Experimental verification for the dynamic discrimination approach**

The developed approach was verified through comparison of AEMP and acid dissolution with atomic-absorption finish (AA) measurements. The results are shown in table 1.

$C_U$ is mass fraction of uniformly distributed element and element in submicron particles. $C_D$ is impurity in discrete particles. In first case (№ 1), the oil sample from D30KP engine (70 um filter cell finesse) was measured. In second case (№ 2), the oil filter wash sample was measured. For each case, 3 concurrent measurements were carried out.
The table 1 shows, that results for AA and AEMP measurements agree within error for both cases. This is evidence that the developed approach to signal extraction allows taking the measurements of samples independently of the content shape, being submicron or coarse particles or metalorganic content.

Table 1. Results of measurements of Fe, Cu in liquid samples using AEMP and AA methods.

| №  | Element | AEMP method | AA method |
|----|---------|-------------|-----------|
|    |         | Cu + Cd = Ctotal, ppm | Ctotal, ppm |
| 1  | Fe      | 2.15+0.80=2.95 ± 1.04 | 3.05 ± 0.31 |
|    | Cu      | 0.04+0.01=0.05 ± 0.04 | 0.06 ± 0.02 |
| 2  | Fe      | 2.25+3.00=5.25 ± 1.79 | 6.07 ± 0.61 |
|    | Cu      | 1.37+1.12=2.49 ± 0.89 | 2.25 ± 0.21 |

6. Conclusion
The mathematical study of analytical signal for AEMP measurements showed that the signal consists of two parts. The first part was shaped by submicron (less than 2 um) particles and metalorganic content, described by random process and resulted in uniform signal. The second part was pulse signal from discrete coarse metallic particles. The suggested “dynamic discrimination” algorithm allowed extracting each part from signal individually, which was verified by comparative AEMP and AA measurements.

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