Pollutant Type: *Particulate Pollutants*

Pollutant/Metric Name: Non-C Elemental Composition

Measurement Technology: Microplasma breakdown spectrometry (LIBS/SIBS/MIPS)

The application of microplasma breakdown analysis to aerosols is known for about three decades [e.g. Radziemski et al. 1983]. Plasma generation by laser pulses, electric sparks and microwaves have been reported so far. The resulting excited atoms in the plasma volume emit specific atomic emissions that can be used to identify elemental composition of aerosol particles.

A) Laser-induced breakdown spectrometry (LIBS)

Laser induced breakdown spectroscopy, possibly first presented by Tomlinson et al. 1966, has found wide application in material analysis. Application to analysis of airborne PM was reported by e. g. Lithgow et al.2004). Recently, considerable progress was reported in application of LIBS to analyse aerosol composition [Hahn 2009].

Figure 1 shows the typical scheme of a LIBS system [Park et al. 2009] along with three variations of aerosol inlets which are needed to focus the particles into a jet which size fits to the focal area of the laser beam. The third possibility collects the aerosol particles on a target prior to vaporisation, leading to an increase of excited atoms and lower (air concentration) detection limits. Moreover, with this approach particles in the ultrafine range (<100 nm) can be measured [Park et al 2009]. By using electrostatic deposition instead of aerodynamic focusing further improvements of precision, accuracy and detection limits are achieved [Diwakar et al. 2012].

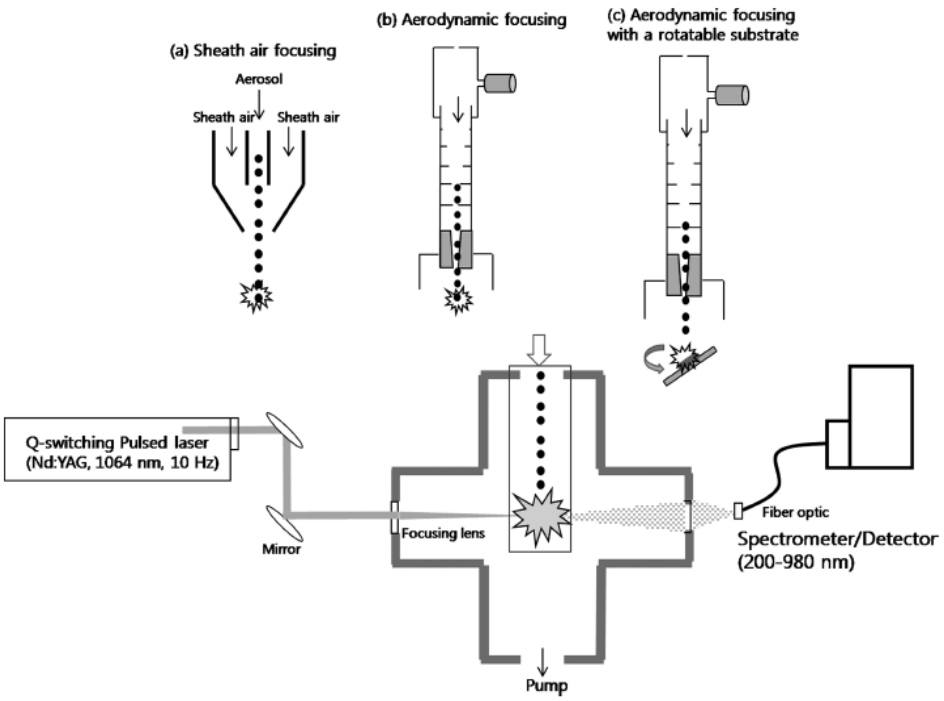

Figure 1: Scheme of LIBS measurements (from [Park et al. 2009], reprinted with permission from Taylor&Frances, www.informaworld.com)

With this method e. g. 10 ng/m³ of copper can be determined within ca. 5 minutes. As the response is element dependent higher detection limits are observed for other elements. Difficulties may arise introduced by matrix effects. The mixture of elements and changes in concentration may lead to changing local plasma conditions [Diwakar et al. 2007] which consequently can bias the simultaneous quantification of internally mixed particles.

b) Spark-induced breakdown spectrometry SIBS

Aerosol analysis by SIBS has first been reported by Hunter et al. 2000 and was developed to achieve emission and workplace monitoring of heavy metals. A more recent application aimed at the detection of biogenic/biological particles against the background of increased needs for protection against biological warfare [Bauer et al. 2006].

The process is illustrated in Figure 2.

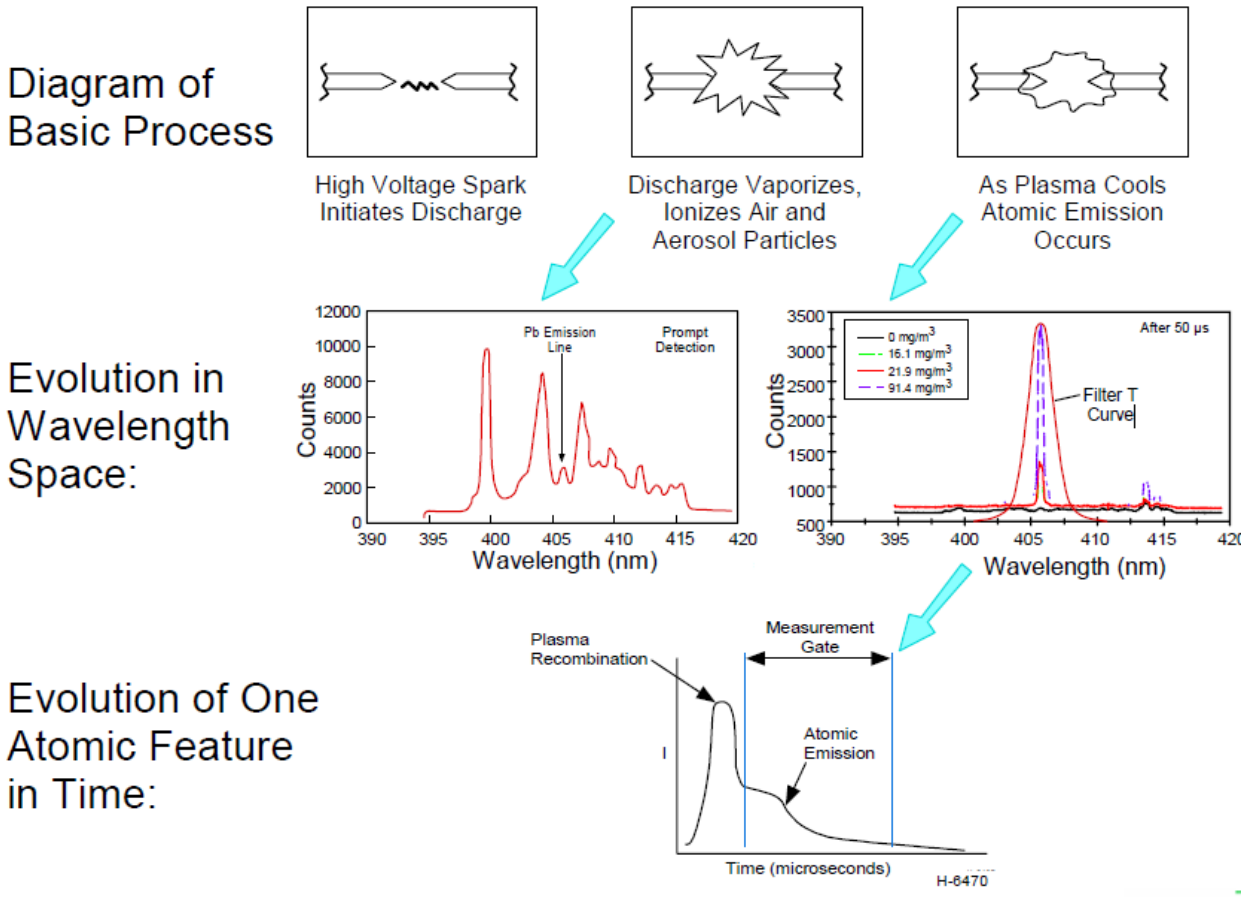

Figure 2: Scheme of SIBS process (taken from Bauer et al. 2006, courtesy of Physical Science Inc.)

The detection limits reported for SIBS still are considerably higher than for LIBS. Thus, while being suitable for emission monitoring (e. g. Ottesen et al. 1991), only elements present in upper ng/m³ or µg/m³ concentrations may be detected in ambient air.

c) Microwave -induced plasma spectrometry (MIPS)

The use of microwave plasma for aerosol breakdown analysis was reported by DUAN et al. 2000. Sensitivity revealed to be lower than for LIBS and the method was therefore applied to emission measurements. Another interesting development is the combination of a microwave plasma with cavity ringdown spectroscopy [Duan et al. 2003].

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Author(s):	Ulrich Quass	IUTA, Germany
Co-author(s)		
Last revision:	24.08.2012	U. Sager/U. Quass, IUTA