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Characterizaction of the sliding spark Plasma source for trace spectroanalysis of dielectric matrices

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CHARACTERIZATION OF THE SLIDING SPARK PLASMA SOURCE FOR TRACE SPECTROANALYSIS OF DIELECTRIC MATRICES

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Summary of Presentation

► Surface Spark Discharges

► Sliding Spark (Plasma)

► Analytical Application

► Selected Results

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► Analysis & Discussion

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Surface Spark Discharges

Research on transient surface discharges is focused mostly on the gas dynamic, electrical and radiative physics applicable to the engineering of novel plasma sources

These have immediate use in low inductance switches, pulsed light sources, optical pumps for intense excimer lasers, and broadband sources of intense UV- VUV radiation.

Hardly is any attention directed to spectroanalytical applications of these sources: However special varieties of surface discharge plasmas propagating on dielectrics in gas/air have potential for trace spectroanalysis of non-conducting matrices and surfaces.

Direct solid-state analysis (hardly available for non-conducting materials) is characterized by many benefits: AES approach is attractive due to its simplicity, rapidity, accuracy, and ease with which it is possible to automate emission spectrochemical analysis.
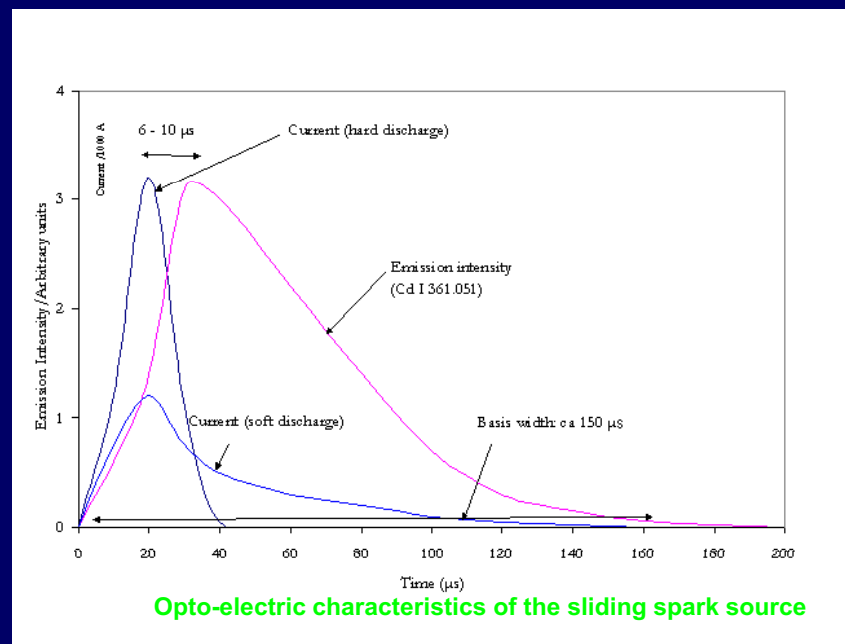
Sliding Spark Plasma (1/2)

Pulsed transient plasma propagating along surface of dielectric matrix enforced between pair of electrodes in air at atm. pressure.

Matrix-excitation driven by geometry- and source opto-electric-, modulated e- impact excitation.

A transient creeping plasma develops in the evanescent depth of dielectric material.

Fast, ablative vaporization is followed by atomization, ionization, excitation of optical emission from elements.

Opto-electric characteristics of the sliding spark source

Short-lived DC arcs develop high power density in a uniform field, and proceed at a considerably lower static breakdown voltage, aided by field perturbations induced by the sample matrix surface microstructure.

Sliding Spark Plasma (2/2)

Dielectric bounds the plasma in one dimension, thus affecting the gas dynamic and radiative properties of the surface in a manner that is distinct from the free spark, the Lichtenberg patterns and the RF 'gliding sparks'.

Due to the small cross section of sliding spark discharge a high electric field potential drop is achieved in a narrow region along the surface of the solid with a discharge brilliance far superior to the free spark operating at the same V and I.

High T_e (17000 K in plasma core) leads to increased vaporization, high particle and η_e, high current density, σ, high resistance per unit length, and short optical pulse.

Matrix excitation accompanied by prompt spectral emission over a broad range (soft X-ray – NIR): As plasma cools, broadband emission decays and are emitted following relaxation of excited matrix species.

LTE is established only after several µs for emission lines in the near UV/VIS range once $T_e \approx 1,0000$ K, and e- densities $\geq 5 \times 10^{22}$ m^{-3} are achieved.

Analytical Application (1/2)
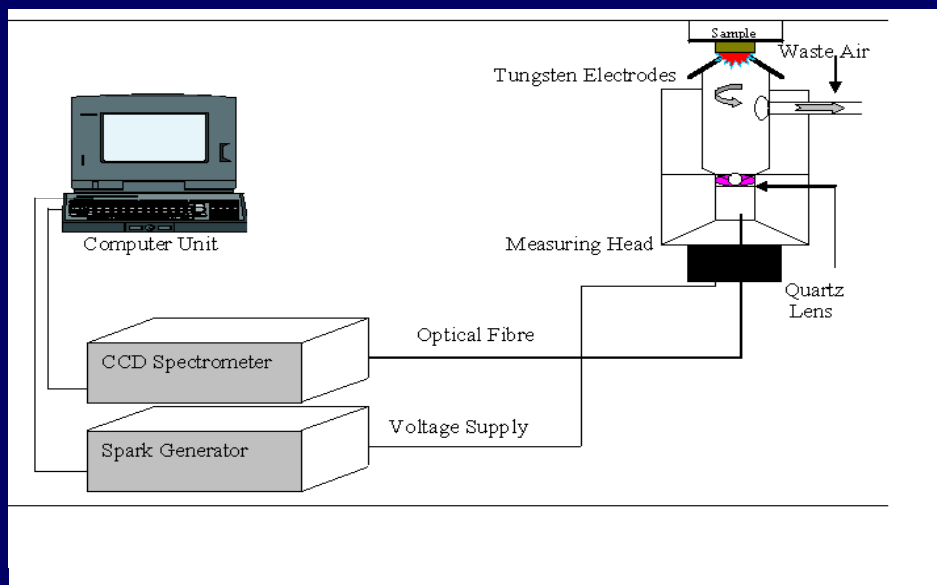
Technical data of the CCD spectrometer employed in the measurements

Grating	Holographic blazed grating	
Grating constant	1600	grooves/mm
Focal length	150	mm
Diameter	20	mm
Blaze	220	nm
Blaze angle α	5	°
Entry slit width	11 & 35	µm
Reciprocal linear dispersion	4.2	nm/mm
Wavelength range	$212 - 511$	nm
3 CCD-(2100 pixel) sensors	UV sensitised one-dimensional array	
Pixel Dimensions (W x H)	14 X 200	µm
Dark current @ 293 K	0.3	mV
Operational voltage	1.8	V
Dynamic range	6000	
Total transfer efficiency	95-97	%
A/D conversion	12	Bit
Dimensions (L x W x H)	20x15x10	cm

Systematic optimization of matrix and spark plasma source parameters leads to the sufficient and necessary (ablative, opto-electric, temporal, geometric, matrix) conditions for realization of optically thin spark plasma suitable for trace analysis of heavy elements embedded in the base dielectric matrix.

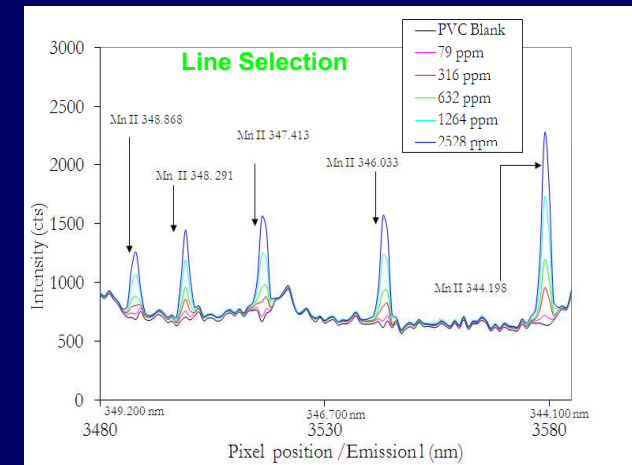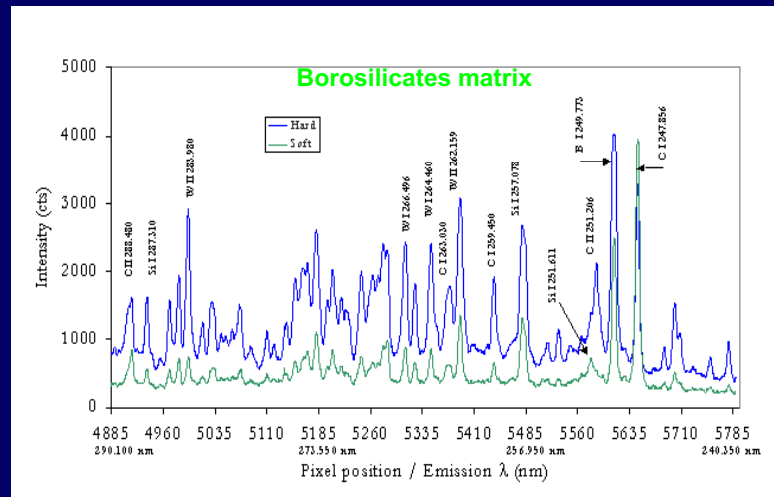**Spiking scheme and analysis conditions for the spark-resolved measurements**

Spark source conditions

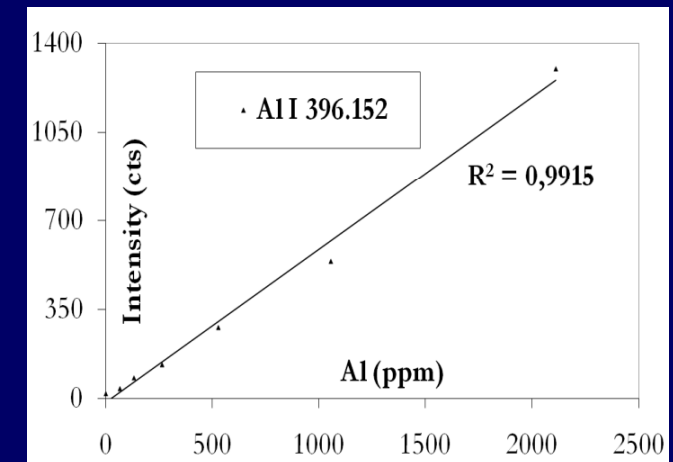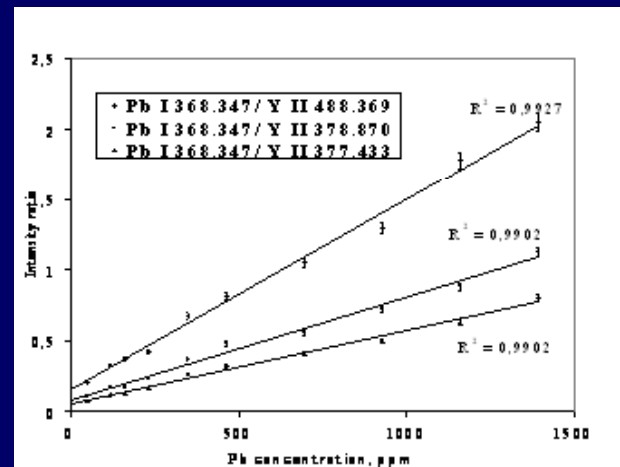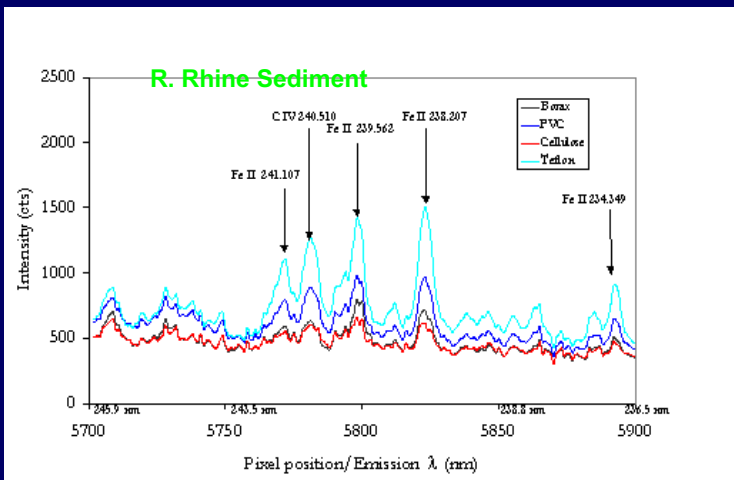|	
Source capacitance	14 µF
Discharge condition	'Hard'
Number of scans	30
Scan time	200 ms, 100 ms
Electrode gap	4.5 mm

Analytical Application (2/2)

Major bands excited in sliding spark in a typical dielectric matrix

| λ (nm)	Molecule	System	Transition
487.30	H₂	Hydrogen	——
486.13	Hᵦ	Hydrogen	——
485.66	H₂	Hydrogen	——
485.65	CH	4300 Å	$A^2\Delta$—$X^2\Pi$
433.66	OH	Schüler-Woeldike.	$B^2\Sigma^+$—$A^2\Sigma^+$
425.22	CN	LeBlanc's	$B^2\Sigma$—$A\Pi$
424.89	CO⁺	Commet-tail	$A^2\Pi$—$X^2\Sigma$
422.53	CH⁺	D-H	$A^1\Pi$—$X^1\Sigma$
402.78	NO	ß-system	$B^2\Pi$—$X^2\Pi$
388.34	CN	Violet	$B^2\Sigma$—$X^2\Sigma$
387.14	CN	Violet	$B^2\Sigma$—$X^2\Sigma$
387.13	CH	3900 Å	$B^2\Sigma$—$X^2\Pi$
386.19	CN	Violet	$B^2\Sigma$—$X^2\Sigma$
385.79	N₂	2⁺ system	$C^3\Pi_u$—$B^3\Pi_g$
385.22	C₂	Desl.-d'A.	$C^1\Pi_g$—$B^1\Pi_u$
385.09	CN	Violet	$B^2\Pi$—$X^2\Sigma$
359.04	CN	Violet	$B^2\Pi$—$X^2\Sigma$
350.30	CH⁺	Violet	$B^1\Delta$—$A^1\Pi$
288.52	NO-ß	ß-system	$B^2\Pi$—$X^2\Pi$
288.50	NH⁺	2885 Å	$C^2\Sigma$—$X^2\Pi$

Borosilicates matrix

Line Selection

Every excited matrix constituent features specific spectral signatures: lines emitted by free atoms, ions, molecules and interference background. Most of the radiation results from early stages of the plasma thermolization, and from electron-ion interaction and recombination.

R. Rhine Sediment

Selected Results (1/2)

CRM (stream) sediment

Mn II 257.610

GBW7311

GBW7307 GBW7306

GBW7305

R0I-02

CRM (sewage sludge)

Mn II 257.610/Y II 378.870

GBW7305

GBW7307 GBW7306

ROI-02
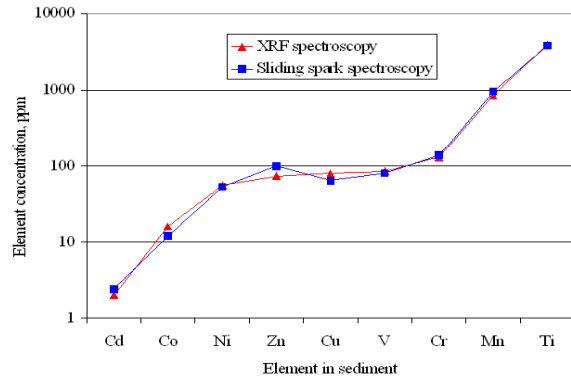
Comparison between the performance of sliding spark spectroscopy against the XRF method, in predicting the concentrations of heavy elements in sediment
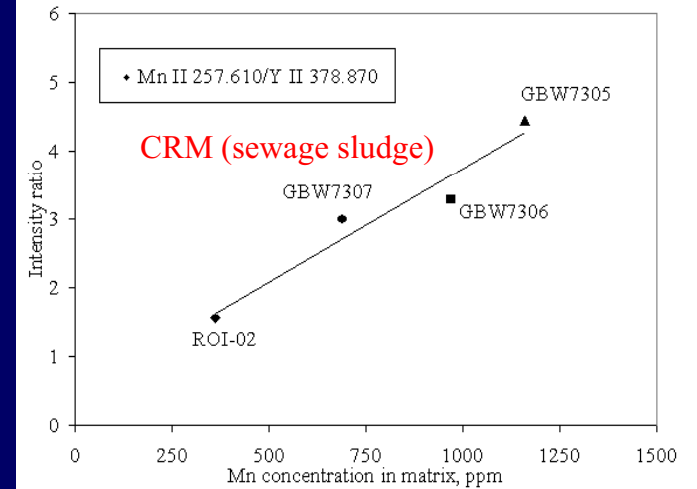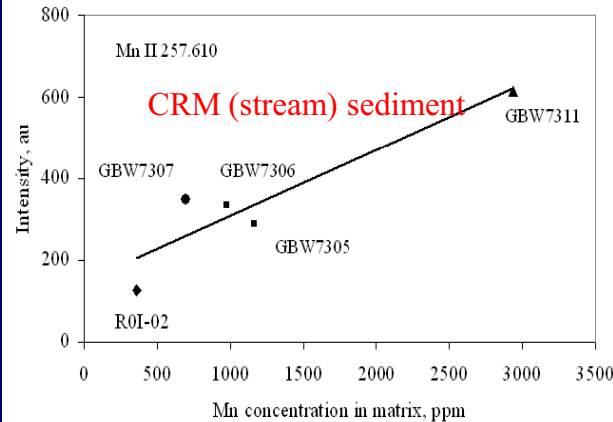
Method Validation for sliding spark spectroscopy by transfer of the developed analytical calibration models for the analysis of some heavy elements in certified reference material GBW-7306 (Chinese Stream Sediment)

Element/line	SAM calibration	SAM with Internal S	Internal Standard line used	External calibration	External calibration with internal Standard	Internal Standard line used	Certified concentration (ppm) or (%)
Ti II 323.452 Ti I 498.173	4010±685 3356±573						4640±180
Zn I 472.216 Zn I 334.502					70.3±10.5	Y II 488.369	144±10
Pb							27±5
Ni I 352.454 Ni I 310.771	52.2 ±5.0				80.9±9.5 86.7±8.5	Y II 378.870 Y II 377.433	78±7
Co II 236.379					30.3±4.6	Y II 354.901	24.4±3.0
V II 297.226					59.9±8.4	Y II 378.870	142.12
Cr I 357.869							190±24
Cd II 226.502					1.63±0.4	Y II 488.369	0.43±0.04
Fe II 274.111	(3.2 ±0.43) %	(3.7±0.57) %		(4.8 ±0.41) %			(4.1±0.07) %
Mn II 260.569	1053±97	1318±131	Y II 488.369				970±60
Cu							383±18
Al I 396.152				(5.3±0.78) %			(7.49±0.07) %

Elemental limits of detection vary from several hundred ppb to few tens of ppm depending on the element, analyzed matrix, spectral line and calibration strategy.

Technique comparable to ICP-AES and EDXRF (polarized, 3-D) in terms of reproducibility ≤ 12 %, precision ± 0.5–10 % , accuracy ≈ 0–10 %.

Selected Results (2/2)

With a proper calibration strategy, based on multi-signal and multivariate spectral approaches, rapid, direct, simultaneous trace quantitative spectroscopy of dielectric solids is feasible utilizing the sliding spark in air at atmospheric pressure as an excitation source.

Analytical utility of the technique depends on the element of interest and matrix.

Use of suitable matrix modifiers results in increased sensitivity.

Internal standards Y and La (added) and Si and C (matrix-derived) lines compensate for differing ablation yield, signal drifts and matrix effects in and between complex matrices.

Accurate analytical models derived for Mn, Ti, V, Ni, Co, Cu, Cd, Pb, Cr, Al, Fe, Zn, and Hg. A quantification methodology developed based on sediment as model matrix.

Method Merits

1. Potential for quantitative and qualitative atomic and molecular spectroscopy.

2. Applicable for simultaneous, *in situ* analysis.

3. A direct solid analysis method applicable to non-conducting materials.

4. Use of optical fiber readily adapts it to remote analysis applications.

5. High flexibility in analytical line selection with possibilities of multivariate calibration

6. Sample preparation is almost absent or easy and does not need any liquid steps.

7. Combines vaporization and excitation is one single step

8. Flexibility in new spark sources design as the power source is simple

9. Potential for speciation analysis, which has become a great challenge.

Method Limitations

1. Subject to extreme matrix effects at minor and major analyte concentrations

2. Suffers from random shot-to-shot variation in the matrix ablation (sampling).

3. High continuum radiation due to bremsstrahlung in emission: spectral overlaps.

4. Essentially a surface-layer, as opposed to surface technique.

5. Spectral broadening due to Doppler, collisional and Stark-effects, due to high density

6. Most of the sensitive analytical lines are plagued by self-absorption and line reversal

Analysis & Discussion (1/2)

Matrix homogeneity is crucial because the mass of sample that is atomized represents only a minute part of the sample.

Because the dielectric matrix is the main source of ions in the plasma, complete vaporization of embedded elements is a pre-requisite for quantitative analysis.

Good SNR may be achievable by gating passed the continuum radiation due to recombination so as to detect only the more persistent analyte emission radiation.

The differences in decay time between ionic an atomic lines can provide a mechanistic insight into, and suggest additional practical applications of, the sliding spark plasma.

Analysis & Discussion (2/2)

Atomic vapour in the post-discharge regions has a lifetime of almost 300 µs following the execution of the excitation pulse, but ionised species reach peak intensity in a few µs.

This means, for quantitative trace spectroscopy it is imperative to find integration times for which good SNR (i.e., use a typical delay time necessary to gate passed the bright continuum radiation due to recombination so as to detect only the more persistent emission radiation of the analyte species excited in the discharge plasma),

And that if the spark source frequency is set to greater than 3 kHz, atomic vapour would continuously be present between the electrodes, and a fluorescence component to the emission is possible.

Hence the sliding spark source at high repetition rates may be optimised to be a vapour source for combined emission, fluorescence, and absorption spectroscopy. Operated under 'soft' discharge mode it would primarily excite few but most intense of the atom lines.

Conclusion

A novel direct spectroanalytical method has been developed based on the sliding spark, where matrix- excitation is driven by plasma particle interaction based on geometry- and source opto-electric-, modulated e-impact excitation to analyse in the in the range (212 nm $\leq \lambda \leq$ 511 nm) using CCD detectors and a blazed holographic grating spectrometer.

The sliding spark is shown as a rich source of excited atoms and ions from the dielectric base matrix, which may be exploited under suitable criteria (e.g., sliding spark-MS).

Sliding spark spectrometry was shown to also detects molecular, including radical species spectra and lots of 'cool' neutral atom species and thus possesses the feasibility for the elucidation of structural and molecular information if temporal gating techniques are used.

Proper opto-electric modulation, optimization of the sliding spark, and use of temporal gating techniques enables the sliding spark as a plasma source of molecular, radical and cold atom species for combined emission, fluorescence, and absorption spectroscopy and for the surface structural elucidation applicable to imaging of dielectric surfaces.

Future Developments

A more comprehensive optimisation of sliding spark spectrometry asks for detailed knowledge on the fundamental processes of sample volatilisation and signal generation.

Applications for micro sliding spark can be envisaged for the study of the spatial relationships of dielectric surfaces (zonation).

Better signal-background ratios may be achieved by optimising the instrument to observe emission either away from or in the discharge axis. Neutral species occur primarily in the cooler wings of the plasma and the ionic emission occurs primarily along the plasma axis.

Time–resolved sliding spark spectroscopy should give a clearer picture of the discharge development with high temporal resolution.

The spark source should be optimised in the physical ablation so that the maximum amount of sample is vaporised with minimum ejection of molten material.

A novel attempt at plasma enhancement would be to surround the plasma with a magnetic field. Influence of magnetic fields on sliding sparks is however so far not studied.

THANK YOU FOR YOUR ATTENTION

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