

## OVERVIEW

### Purpose:

- The development of an accurate LDTD-MS/MS method for a pharmaceutical diclofenac with precision
- This technique omits the chromatographic step and quantifies the sample in 10 seconds.

### Method:

- Diclofenac spiked in wastewater (WW) and wastewater sludge (WWS) samples
- Solid phase extraction (SPE) of wastewater samples using C<sub>18</sub> cartridges
- Calibration range: 1–50 µg/L
- LDTD-APCI-MS/MS analysis: Laser Diode Thermal Desorption coupled with tandem mass spectrometer

## INTRODUCTION

Diclofenac (DCF) is an extensively used non-steroidal anti-inflammatory drug and is among the most frequently detected pharmaceutical compounds in municipal wastewater treatment plants. For the past several years, DCF has been an environmental concern due to its frequent occurrence in drinking water sources. There are not many rapid and advanced methods for the quantification of diclofenac in wastewater (WW) and wastewater sludge (WWS) due to its low concentrations and complexity of the wastewater matrix.

A MS interface LDTD combined with atmospheric pressure chemical ionization (APCI), has shown great potential to reduce analysis time from minutes to seconds by removing the chromatographic step and introducing charged analytes directly into the mass spectrometer.

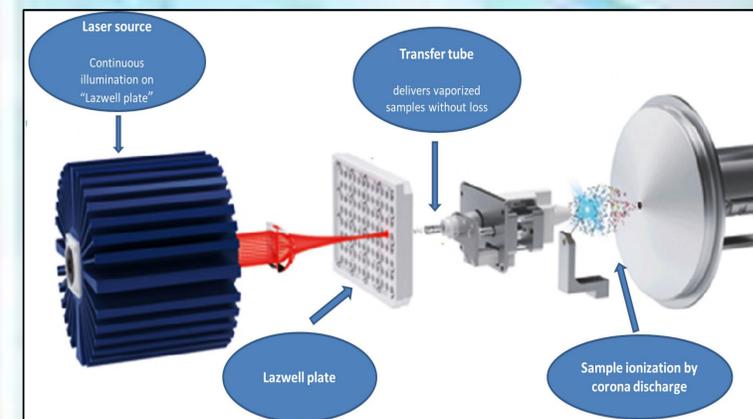


Figure 1: Schematic of LDTD ionization source

## METHOD

### Sample Preparation

- Centrifugation of sludge sample
- Lyophilization of solid residue
- Microwave extraction of lyophilized solid

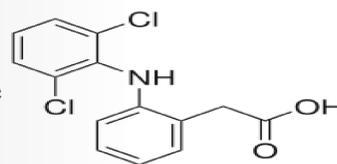


Figure 2: DCF chemical structure

### Clean up

- SPE of sample using C18 cartridges and methanol/acetonitrile mixture (50 : 50, v/v) as eluent
- Dry the extract under a gentle stream of N<sub>2</sub>
- Dried residue was reconstituted with 1 mL of acetonitrile before analysis
- Add Na<sub>2</sub>H<sub>2</sub>EDTA to the sample to make DCF free from metal complex

### Instrumentation:

- LDTD T-960, Phytronix Technologies
- Thermo Vantage Mass Spectrometer

### LDTD Parameters

- Laser power pattern :  
The laser power is ramped from 0 to 65% in 6.0 s and hold at 65% for 2.0 s
- Carrier gas (Air) temperature: 30 °C and flow rate :3 L/min
- The optimum sample volume deposited into a well is 4 µL

### Mass Spectrometry parameters

- Ion source :APCI (-)
- Mode: SRM
- DCF: 296,2 -> 215,0  
298,0 -> 215,0
- DCF-d4: 300,0 -> 219,0  
302,0 -> 219,0



Figure 3: LDTD-MSMS analytical system

## RESULTS

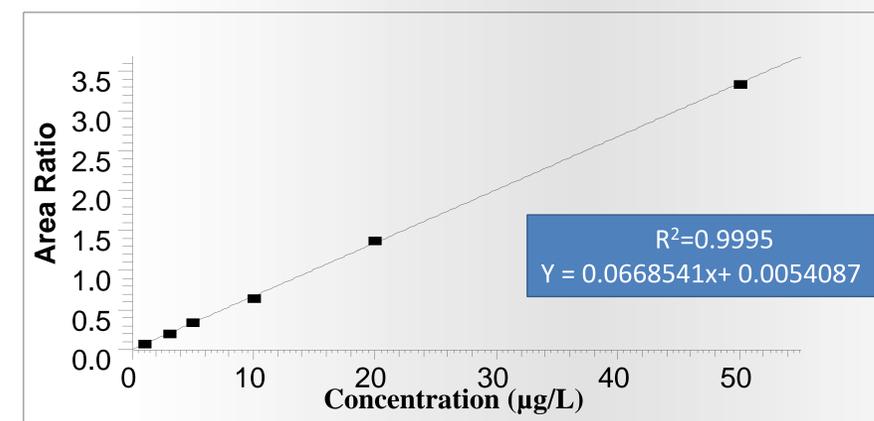


Figure 4: Calibration curve of DCF

Table 1: Diclofenac method validation parameters with wastewater and sludge

R <sup>2</sup>	Intra-day precision	Inter-day precision	MDL (ng/L)	
	(%RSD)	(%RSD)	LOD	LOQ
0.9995	7.1	9.2	270	1000

Table 2: Concentrations of diclofenac in wastewater samples collected from Quebec Urban Community (QUC) WWTP (n = 3)

Sample ID	Concentration ±%RSD (n=3) (µg/L)	Sample ID	Concentration ±%RSD (n=3) (µg/g)
Influent	1297.8±88	Primary sludge	22±6
Primary wastewater	698.2±20	Secondary sludge	18±8
Secondary wastewater	489.6±60	Effluent	319±12 µg/L

## DISCUSSION AND CONCLUSIONS

- A simple, rapid and sensitive method was developed for the quantification of DCF in wastewater samples.
- Method was tested with the analysis of DCF in wastewater and wastewater sludge for applicability for environmental samples
- Recovery for DCF ranged from 87% to 99% for the samples
- The method demonstrated acceptable precision and accuracy across the calibration range of interest.

### Acknowledgement

We thank NSERC Strategic grant for the financial assistance. The help of Phytronix Inc. team in analysis of diclofenac using LDTD-MS/MS is also highly appreciated