# Cloud point extraction and pre-concentration of chromium for environmental analyses

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## Introduction:

- Chromium (Cr) is a metallic element used in many alloys (such as corrosion-resistant steels), colorful pigment compounds in certain paints, in leather making, and in wood preservatives
- Trace chromium(III) (ions with Cr in +3 oxidation state) are essential to animals and humans
- Large amounts of chromium(III) is harmful, chromium(VI), or "hexavalent chromium", is a known carcinogen
- Measuring the (usually) very low concentrations of Cr in environmental samples is difficult without expensive instrumentation like inductivel-coupled plasma atomic emission spectrometers (ICP-AES)
- To utilize available instruments at LMU like the flame atomic absorption spectrometer (AAS), we need a method to extract and concentrate the Cr
- Compared to regular solvent extraction, cloud-point extraction is chosen as a "green" method, minimizing waste and harmful organic solvents

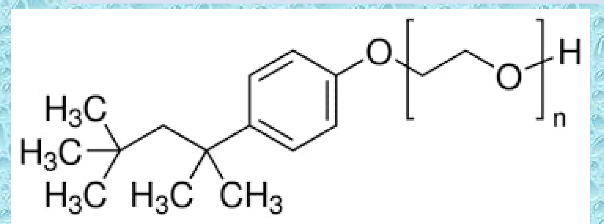


**Figure 1 (above):** Shorthand structure for surfactant molecules in Triton X-100

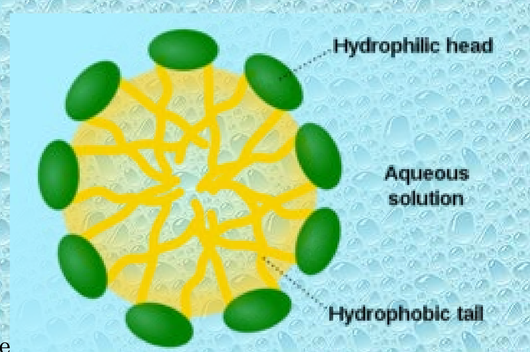



**Figure 2 (right):** Structure of surfactant micelle. Hydrophobic portions form a nonpolar interior phase

## Surfactant micelles:

- Surfactants are long organic molecules with one part being hydrophilic ("water-loving"), and another being hydrophobic ("water-fearing")
- Nonionic surfactants like Triton X-100 (Fig 1) have a nonpolar aromatic and branched hydrocarbon for the hydrophobic "tail" and a polar poly(ethylene glycol) = PEG chain for the hydrophilic "head"
- Surfactant molecules aggregate into micelles, with hydrophobic tails in center, hydrophobic heads on the outside (Fig 2)
  - This occurs above the critical micelle concentration (cmc)

## Cloud point extraction (CPE):

- The cloud point phenomenon is observation that a concentrated surfactant solution of micelles undergoes phase separation when heated above a certain temperature (the cloud point or CP)
  - One phase (viscous) is rich in surfactant micelles; second phase is mostly aqueous
  - Droplets of the viscous phase makes the clear solution look cloudy / milky
- First part of extraction is to add a reagent or ligand to form a hydrophobic complex with the species of interest (see Fig 3)
  - For Cr in 3+ state, suitable ligands include bis-2-[hydroxynaphthaldehyde] thiourea, brilliant cresyl blue (BCB) and 1,5-diphenylcarbazide (see Fig 4 below)
  - Cr in +6 state is usually reduced to +3 state by reductants like ascorbic acid
- Surfactant at sufficiently high concentration is used to create micelles
- Hydrophobic complex is preferentially absorbed into surfactant micelles
- Heating system above cloud point causes phase separation
- Centrifugation and removal of supernatant aqueous phases leaves concentrated "rich" phase in tube
- Water and salt used to redissolve "rich" phase with much higher Cr concentration

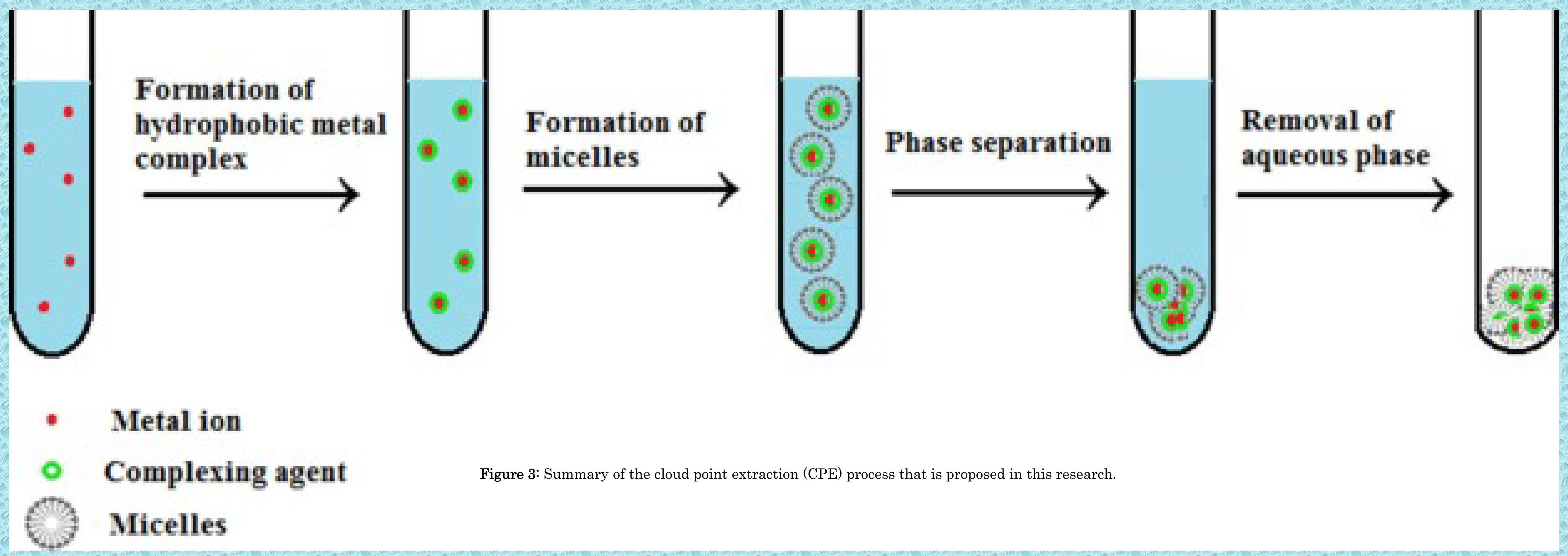
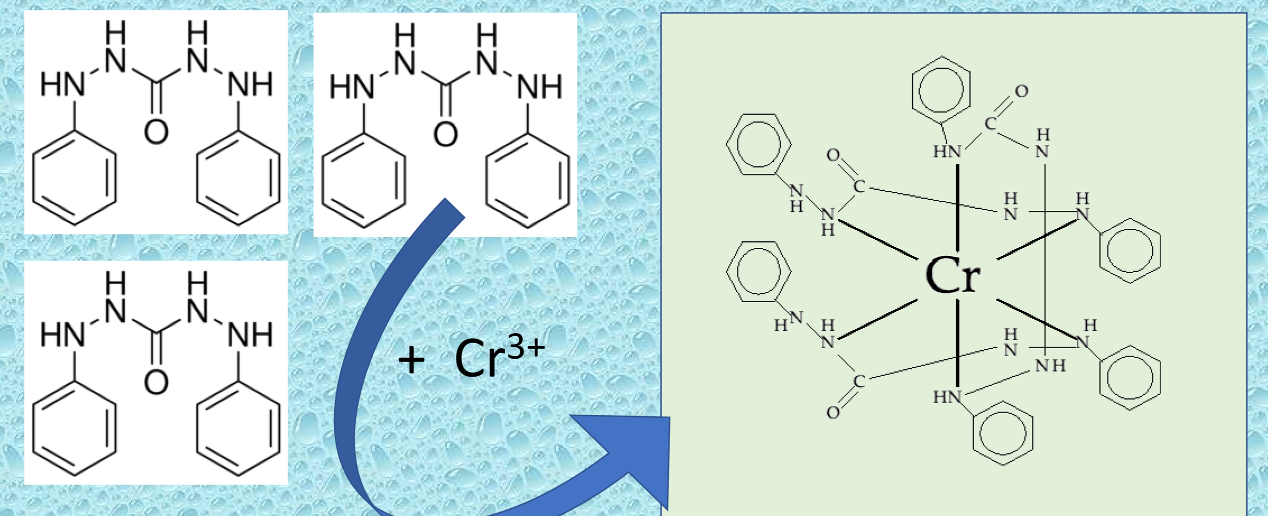



**Figure 3:** Summary of the cloud point extraction (CPE) process that is proposed in this research.

**Figure 4 (below):** Complexation of chromium(III) ion with three ligand molecules (1,5-diphenylcarbazide) to form neutral and hydrophobic complex for extraction into Triton X-100 micelles.




## Equipment and materials:

- Chromium extracted will be measured by our Shimadzu AA-6300 flame atomic absorption spectrometer (AAS, Fig 5) using existing Cr lamp and burner head
- A standard laboratory centrifuge (Fig 6) will be used for phase separation once system heat above the cloud point temperature
  - Extracts mixed with ligands and surfactant in centrifuge tubes
- Surfactants to investigate:
  - Key nonionic is Triton X-100
  - Others to investigate include Triton X-114, Tween-20, Igepal CA-360
- Ligands to investigate:
  - Key is 1,5-diphenylcarbazide
  - Others to investigate include bis-[2-hydroxynaphthaldehyde] thiourea and brilliant cresyl blue stain
- Salts like NaCl added to investigate ionic strength effects
- Hotplate for heating systems (in centrifuge tubes and water baths), may consider thermostatted water baths


**Figure 5 (above):** Shimadzu atomic absorption spectrometer (AAS) with flame atomization for Cr concentration determinations.

**Figure 6 (right):** Standard laboratory centrifuge to enable extraction of the micelle-rich phase after phase separation beyond the cloud point.

## Investigations and anticipated results:

- Will investigate the surfactant structure effects on efficiency of extraction of Cr from environmental samples and standard samples
  - Expect surfactants with more dominant hydrophobic tails to be better at extraction
  - High surfactant concentration likely to be more effective up to certain point
- Will investigate effectiveness of different ligands
  - Key ligand (1,5-diphenylcarbazide) expected to be most efficient due to common use in trace Cr analyses
- Other factors like heating time, temperature, and ionic strength will be investigated