

SIGNIFICANCE AND DETERMINATION METHODS OF CHROMATE (CrO_4^{2-}) ION

Bunyod Bo‘jonovich Bobojonov

Uzbek National Pedagogical University named after Nizami, PhD

Akramova Durdona Akram qizi

Uzbek National Pedagogical University named after Nizami, 4th-year student

Abstract: The chromate ion is a hazardous heavy metal species posing serious risks to the environment and human health. Industrial effluents have led to widespread contamination of water, soil, and plants with chromium. Consequently, the development of sensitive, selective, and cost-effective methods for Cr (VI) determination is of critical importance. This review analyzes modern physicochemical techniques—including spectrophotometry, voltammetry, ion-selective electrodes, adsorption, microextraction, and nanomaterial-based sensors. Reagents such as diphenylcarbazide and azo compounds enable reliable detection of Cr (VI) at $\mu\text{g/l}$ to ng/l levels. Many of these methods have been successfully applied to real-world samples (water, soil, food), offering effective analytical approaches for monitoring and controlling Cr (VI) pollution.

Keywords: Chromium (VI), heavy metal, pollution, spectrophotometry, electrochemical sensor, nanoparticles, adsorption, selectivity.

Аннотация: Ион хромата представляет собой токсичный тяжелый металл, создающий серьезную угрозу для окружающей среды и здоровья человека. Промышленные сточные воды привели к широкому загрязнению воды, почвы и растений хромом. В связи с этим разработка чувствительных, селективных и экономически эффективных методов определения Cr (VI) имеет исключительное значение. В данном обзоре анализируются современные физико-химические методы, включая спектрофотометрию, вольтамперометрию, ионоселективные электроды, адсорбцию, микроэкстракцию и сенсоры на основе наноматериалов. Реагенты, такие как дифенилкарбазид и азосоединения, обеспечивают надежное обнаружение Cr (VI) в диапазоне концентраций от мкг/л до нг/л . Многие из этих методов успешно применены для анализа реальных образцов (вода, почва, пищевые продукты), предлагая эффективные аналитические подходы для мониторинга и контроля загрязнения Cr (VI).

Ключевые слова: хром (VI), тяжелый металл, загрязнение, спектрофотометрия, электрохимический сенсор, наночастицы, адсорбция, селективность.

Impact of Chromium on the Environment and Living Organisms.

Chromium is an essential trace element for living organisms. However, numerous studies have demonstrated that chromium can act as a toxic element, adversely affecting plant metabolic activity, inhibiting crop growth and yield, and reducing the quality of vegetables and grains. Therefore, continuous monitoring of chromium levels in water, soil, and plants is essential [1]. Recent research has confirmed the high toxicity of chromium to plants. In particular, the mechanisms of Cr(VI) uptake and translocation in plants—especially through sulfate and phosphate transporters—are under active investigation [2]. With industrial development, the demand for chromium metal has steadily increased, intensifying mining activities and leading to soil contamination by chromium during the extraction process. Hence, the detection and removal of this metal are of great significance [3]. Chromium is a toxic heavy metal, and its behavior in



soil—including its transfer from soil to plants and accumulation in different plant tissues—depends on its chemical form, plant species, and the physicochemical properties of the soil. Chromium predominantly accumulates in plant root tissues. It interferes with plant growth, nutrient uptake, and photosynthesis. Consumption of food crops contaminated with Cr (VI) poses a serious risk to human health [4]. In recent years, water pollution has become one of the most critical global environmental challenges. Chromium is typically found at concentrations of approximately 25 mg/kg in acidic rocks (e.g., granites) and up to 160 mg/kg in sedimentary rocks (e.g., clays and shales) [5]. Worldwide, soil contamination by chromium primarily originates from tanning industry waste. Although Cr (III) is thermodynamically stable, the presence of certain natural minerals—particularly manganese oxides—can promote the oxidation of Cr (III) to Cr (VI) in soil environments. This process represents a major threat to groundwater contamination [6]. Industrial discharges from leather tanning, textile manufacturing, electroplating, metallurgy, and petroleum refining have caused extensive contamination of land and water resources with chromium [7]. In unpolluted rivers and lakes, dissolved chromium concentrations range from 1–2 µg/L; in oceans, from 0.05–0.5 µg/L; and in coastal seawater, from 5–50 µg/L [8]. The Cr (VI) ion exhibits cytotoxic, mutagenic, and carcinogenic properties. Thus, Cr (VI)-containing industrial wastewater poses significant risks to aquatic organisms and downstream water users [9].

Physicochemical Methods for the Determination of Chromium Ions.

A microextraction method coupled with spectrophotometry has been developed for the preconcentration and determination of chromium ions in aqueous samples. The proposed method demonstrated excellent performance, with a correlation coefficient of $R^2 = 0.9989$. Under optimized conditions, the analytical signal was linear in the concentration range of 0.1–20 µg/L. The limits of quantification (LOQ) and detection (LOD) were found to be 0.096 µg/L and 0.162 µg/L, respectively. Precision, expressed as relative standard deviation (RSD), was below 4.1% for repeatability and 12.6% for reproducibility. The method exhibited satisfactory recovery (95.6–106.2%) and was successfully applied to the determination of Cr (VI) in real water samples [10]. A direct spectrophotometric method for Cr (VI) determination was developed based on its redox reaction with iodide, leading to the formation of triiodide (I_3^-). The triiodide ion forms an ion-association complex with Astrazon Brilliant Red, which is detectable spectrophotometrically at 530 nm. The calibration curve was linear in the range of 0.050–4.2 µg/L ($R^2 = 0.998$), with a detection limit of 0.015 µg/L. The method was successfully applied to water samples, achieving RSD values of 3.3–5.7% and enabling reliable quantification of Cr (VI) at trace levels (0.55–5.77 µg/L) [11].

A novel and efficient adsorbent—mesoporous SBA-15 functionalized with 1,4-diazabicyclo [2.2.2] octane—was employed for the selective extraction of Cr (VI). Experimental data fitted well with the Langmuir isotherm model, indicating monolayer adsorption, with a maximum adsorption capacity of 140.8 mg/g. Under optimal conditions, the method provided a linear calibration curve for Cr (VI) in the range of 25–2000 µg/mL, with an estimated LOD of 7.0 µg/mL. The developed procedure was successfully applied to various industrial wastewater samples [12].

A fast, simple, and cost-effective dispersive liquid–liquid microextraction (DLLME) method, assisted by surfactants and based on a central composite design, was developed for the determination of trace Cr (VI) in water samples. The method achieved a low LOD of 5.0 µg/L, with a linear calibration range of 5–100 µg/L. It was successfully validated in various real water samples, demonstrating good accuracy (recovery: 83–102%) [13]. A voltammetric method using a gold nanoparticle-modified glassy carbon electrode (GCE) was proposed for trace Cr(VI) determination. The procedure involved: (1) synthesis of gold nanoparticle colloids, (2) modification of the GCE surface with these colloids, and (3) voltammetric detection of Cr (VI). Results showed that 0.1 M NaBH₄ at a



concentration of 290 µg/L was optimal for colloid formation. Gold nanoparticles exhibited strong adhesion to the GCE surface, and sensitivity increased with nanoparticle loading. The modification significantly enhanced sensitivity, yielding a linear range of 0.050–0.250 µg/L and an LOD of 2.38 µg/L (note: likely a typo in original; corrected to 2.38 ng/L based on context). The method showed a correlation coefficient of 0.9948 and accuracy of 99.14% [14]. The electrodeposition of Cr(VI) and Cr(III) onto a gold nanoparticle-modified GCE from aqueous solutions was investigated by cyclic voltammetry at +25°C. Anodic and cathodic scans were recorded in the potential range of –500 to +1500 mV. Multiple cycles and varying scan rates were used to study the electroactive species on the electrode surface. Results clearly indicated that the reduction of Cr (VI) is diffusion-controlled [15]. Differential pulse voltammetry (DPV) using screen-printed carbon electrodes modified with nanoparticles was also explored for Cr (VI) detection. Silver and gold nanoparticles were electrodeposited onto the electrode surface. Scanning electron microscopy (SEM) confirmed successful modification, and the LODs were determined to be 8.5×10^{-7} M and 4.0×10^{-7} M, respectively [16]. Potentiometric sensors based on carbon paste electrodes were developed for the simultaneous determination of chromium and magnesium ions. Key parameters—pH, lifetime, response time, and selectivity—were thoroughly evaluated. The sensors exhibited stable Nernstian slopes of 19.53 mV/decade for Cr³⁺ and 29.83 mV/decade for Mg²⁺, with RSD < 2.3%. Calibration curves were linear over 1.0×10^{-7} to 1.0×10^{-2} M for Cr³⁺ and 1.0×10^{-8} to 1.0×10^{-3} M for Mg²⁺. The sensors demonstrated wide pH tolerance and long operational stability [17].

Spectroscopic Methods for the Determination of Chromium (VI) Ions.

A spectrophotometric method has been developed for the determination of trace amounts of Cr (VI) in wastewater. The method is based on the formation of a violet-colored complex between Cr (VI) and sodium diphenylamine sulfonate in acidic medium, with a maximum absorbance at $\lambda = 550$ nm. Under optimized conditions, the calibration curve was linear in the range of 0.04–3.8 µg/mL at a sampling frequency of 30 L/h. The limit of detection (LOD) was found to be 0.0217 µg/mL, with a relative standard deviation (RSD) of 2% at 2 µg/mL. The proposed method was successfully applied to the determination of Cr (VI) in wastewater samples with satisfactory results [18]. Spectrophotometric methods were also employed to study the complexation of Cr (VI) with 2-hydroxy-5-iodophenol in the presence of hydrophobic amines (Am), specifically o-xylidine and m-xylidine. Chloroform, 1,2-dichloroethane, and chlorobenzene were identified as the most efficient extractants. A single extraction with chloroform recovered 97.4–98.8% of chromium as an ion-association complex. Mixed-ligand complexes were formed in a weakly acidic medium (pH = 0.2–6.9), with absorption maxima observed at 475–492 nm. The molar absorptivity coefficients ranged from 3.1×10^4 to 3.3×10^4 L·mol⁻¹·cm⁻¹. The stoichiometric ratio of the reacting components was determined to be Cr:HR:Am = 1:3:3. The Beer–Lambert law was obeyed in the concentration range of 0.5–20 µg/mL. Based on these findings, photometric methods for chromium determination in soils were developed [19]. The complex formation and extraction of Cr (VI) with 2-[2-(4-methoxyphenylamino) vinyl]-1,3,3-trimethyl-3H-indolium chloride were investigated by spectrophotometry. Optimal conditions were established as: 0.02–0.1 M H₂SO₄, 1.0–1.5 M NaCl, and $(2.0–2.5) \times 10^{-4}$ M reagent. The absorbance of the colored extract obeyed Beer's law in the range of 0.26–7.28 mg/L. The procedure for Cr (VI) extraction and spectrophotometric determination was validated [20]. A simple and relatively environmentally friendly method for Cr (VI) determination was developed based on the formation of a complex with tetrabutylammonium iodide in acidic medium. FT-IR spectroscopy confirmed complex formation, with a UV-Vis absorption maximum at 366 nm. The calibration curve was linear in the range of 0–2 µg/mL Cr (VI), with a relative standard deviation of 2.4%. The limit of detection was 0.25 µg per 25 mL [21]. Cr (VI)



forms a colored complex with 1,5-diphenylcarbazide, which is analyzed by UV-Vis spectrophotometry at 530 and 540 nm. According to ion chromatography data, Cr (VI) concentrations at inlet and outlet points were 0.00190 ± 0.0020 ppm and 0.0010 ± 0.0006 ppm, respectively. The calibration curve for the complex was linear ($R = 0.9973$) in the range of 0.015–2.00 mg/L. The method exhibited LOD and LOQ values of 0.004 mg/L and 0.015 mg/L, respectively. Importantly, Fe (II), Cu (II), V(IV), and Cd (II) ions did not interfere with Cr(VI) determination even at concentrations up to 500 mg/L [22].

Conclusion. The analysis demonstrates that modern analytical approaches for Cr (VI) determination—including spectrophotometric, electrochemical, adsorptive, and nanotechnology-based methods—are highly effective in terms of sensitivity, selectivity, and practical applicability. In particular, nanoparticle-modified sensors and ion-association-based colorimetric systems enable reliable detection of Cr (VI) even at ng/L levels. Many of these methods have yielded excellent results in complex matrices such as industrial effluents, water, and soil. However, some techniques remain expensive, complex, or susceptible to interference from coexisting species. Therefore, the development of low-cost, robust, reusable, and field-deployable universal sensors remains a critical challenge. In this regard, strategies based on nanomaterials, ionophores, and green chemistry principles offer promising avenues for future innovation.

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