phenolazorhodanine, pyridine-2-aldehyde-2-furoylhydrazone, phenolazotriaminorhodanine, and benzolazobenzolazorhodanine have been proposed for selective detection of toxic heavy metals at nanogram levels. Radiometry is used to detect Pr(III), Pr(IV), and Tb(III). Aluminum ions with high sensitivity at the ppb level have been selectively detected by measuring the fluorescence of complexed Al. The use of square-wave anodic stripping voltammetry as a direct on-plate detection method for Cd^{2+}, Cu^{2+}, and Pb^{2+} (detection limit of each cation, less than 10 ng) was reported by Dewald et al. (56).

B. Anions

For the detection of anions, saturated silver nitrate solution in methanol, 0.2–0.5% diphenylamine solution in 4 mol/L H_2SO_4, 1% aqueous solution of potassium ferrocyanide, 0.5% alcoholic solution of pyrogallol, 10% $FeCl_3$ solution in 2 mol/L HCl, 1% KI in 1.0 mol/L HCl, and a mixture of aqueous KSCN and $SnCl_2$ in 1.0 mol/L HCl, ammonical $AgNO_3$, aqueous bromocresol green, $FeSO_4$ + $FeCl_3$, alizarin, benzidine solution, $(NH_4)_2$ MoO_4 + $SnCl_2$ and 0.1% bromocresol purple containing diluted NH_4OH have been used. Autoradiography, scintillation counting, and radiometric detection methods have also been applied.

C. Rare Earth Elements

The rare earth elements (REEs) have been detected by first spraying the plate with 0.1% arsenazo(III) solution and then with aqueous ammonia followed by gentle heating; second, heating at 70°C for 10 min after spraying with 0.02% chlorophosphonazo solution and then 0.5 mol L^{-1} Hcl; and third, exposure of the plate to NH_3 after spraying with tribromochlorophosphonazo or xylenol orange solution. Saturated ethanolic solution of alizarin and dilute solutions of tribromoarsenazo (0.2–1%) have been used to detect REEs.

D. Metal Complexes

Most metal complexes, being colored, are visible without further treatment. Metal oxinates; some geometrical isomeric complexes of Rh, Pt, and Co methylbenzyldithiocarbamate metal chelates; Cu(II) carboxylates; and Co (glycine) are self-colored but can be located under ultraviolet light. β-Diketonates of Fe, Cr, and Co; organotin compounds; alkali metal xanthates; and piperidine dithiocarbamate complexes can be detected with iodine vapor. The colorless diethyldithiocarbamate complexes of Cd^{2+}, Hg^{2+}, Pb^{2+}, and Zn^{2+} are visualized as yellow-green chelates after spraying the TLC plates with 5% $CuSO_4$ solution. A fluorometric method has been used for the detection of heavy metal complexes with pyrene-substituted *N*-acylthiourea. Sometimes spots are detected by spraying colored reagents such as pyrocatechol violet or copper sulfate or by immersing the TLC plates in a dilute solution (0.05%) of phenylfluorone reagent. *N,N*-Diethyl-*N'*-benzoylthiourea–metal chelates have been detected by graphite furnace atomic absorption spectrometry and by UV detection.

VI. QUANTIFICATION

The three main approaches related to quantitative TLC are (a) visual estimation and spot-size measurement, (b) zone elution and spectrophotometry, and (c) in situ densitometry.

A. Visual Estimation and Spot-Size Measurement

Visual estimation and spot-size measurement is the simplest form of semiquantitative analysis; its accuracy and reproducibility fall in the range of 10–30%. A definite volume of sample is chromatographed alongside standards containing known amounts of analyte. After detection, the weight of analyte in the sample is estimated by visually comparing the size and intensity of the sample zone with the standards. The visual comparison works well if the applied amounts of sample are kept close to the detection limit and the sample is accurately bracketed with standards.