Principal Component Regression (PCR)

Chemometric data description

The data in mat file format contains

1. spectra of each species for wavelengths ranging from 300nm to 650nm with an interval of 2nm.
2. The concentration of each species in the solvent is different from one another.
3. The data also contains spectral profile of mixtures of three species at varied concentrations.
4. There are three concentration levels for each species considered for preparing the mixture.
5. There are five experiments done for each mixture and hence, the data contains 130 samples of absorbance data for 26 mixtures.

In [1]:
```
import numpy as np
from scipy.io import loadmat
from matplotlib.pyplot import *
import pandas as pd

mat_data = loadmat('data.mat')  # load mat-file
wavelengths = mat_data['WAV'][0]  # dictionary element with the key = 'WAV' is a list of list.
species=['Cr','Ni','Co'] # Name of the species in the order specified in the data
species_con=pd.DataFrame(np.concatenate([mat_data['PureCrCONC'],mat_data['PureNiCONC'],
                                         mat_data['PureCoCONC']],axis=1),columns=species)
species_abs=pd.DataFrame(np.concatenate([mat_data['PureCr'],mat_data['PureNi'],
                                         mat_data['PureCo']],axis=0),
                         columns=wavelengths,index=species)
# concentration of each species in the mixtures (each repeated 5 times) - corresponds to Y/output
mixture_con = pd.DataFrame(mat_data['CONC'],columns=species)
mixture_abs = pd.DataFrame(mat_data['DATA'],columns=wavelengths)  # absorbance data for each wavelength corresponds to X/input
```

Concentration of species for absorbance measurement

In [2]:
```
species_con
```

Out[2]:

	Cr	Ni	Co
0	0.0764	0.1965	0.172

Absorbance spectra of each species at the given concentration

In [3]:
```
species_abs
```

Out[3]:

	300	302	304	306	308	310	312	314	316	318	...	632	634	636	638	640
Cr	0.290314	0.277074	0.248891	0.255931	0.282883	0.297658	0.239670	0.307846	0.387466	0.500966	...	0.473480	0.452260	0.428558	0.405090	0.379664
Ni	0.169520	0.161845	0.140849	0.163610	0.200663	0.182780	0.207169	0.294027	0.400558	0.557912	...	0.278854	0.289174	0.303482	0.309128	0.313848
Co	0.373698	0.415131	0.308090	0.342158	0.344152	0.291692	0.268926	0.333201	0.411865	0.581156	...	0.053933	0.052933	0.051943	0.051567	0.050267

3 rows × 176 columns

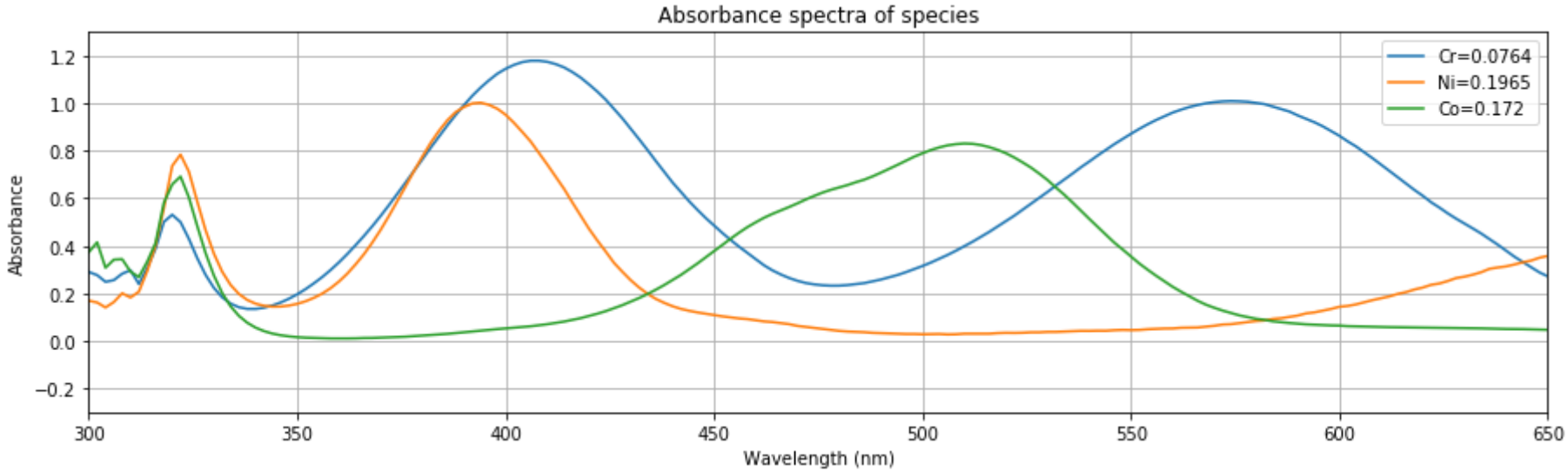
Function to plot the spectra

In [4]:

```
'''
Function to plot spectra
Arguments: df (pandas.DataFrame), labels (list), header (string), vlines (boolean)
Returns: NoneType
'''
def plot_spectra(df,labels,header,vlines):
  fig, ax = subplots(figsize=(15,4))
  df.plot(ax=ax)
  ax.legend(labels,loc='best');
  ax.grid(True)
  ax.set(title=header,xlabel='Wavelength (nm)',ylabel='Absorbance')
  ax.set_ylim(-0.3,1.3)
  if vlines:
    vlines={408:'b',394:'orange',512:'g',574:'b'}
    for i in vlines:
      ax.axvline(x=i,color=vlines[i]) # drawing a blue vertical line at 408nm
      ax.text(i+1,0.6,str(i),rotation=90)
        # writing the wavelength value corresonding to the vertical line and placing the text vertically rotated
```

Species spectra

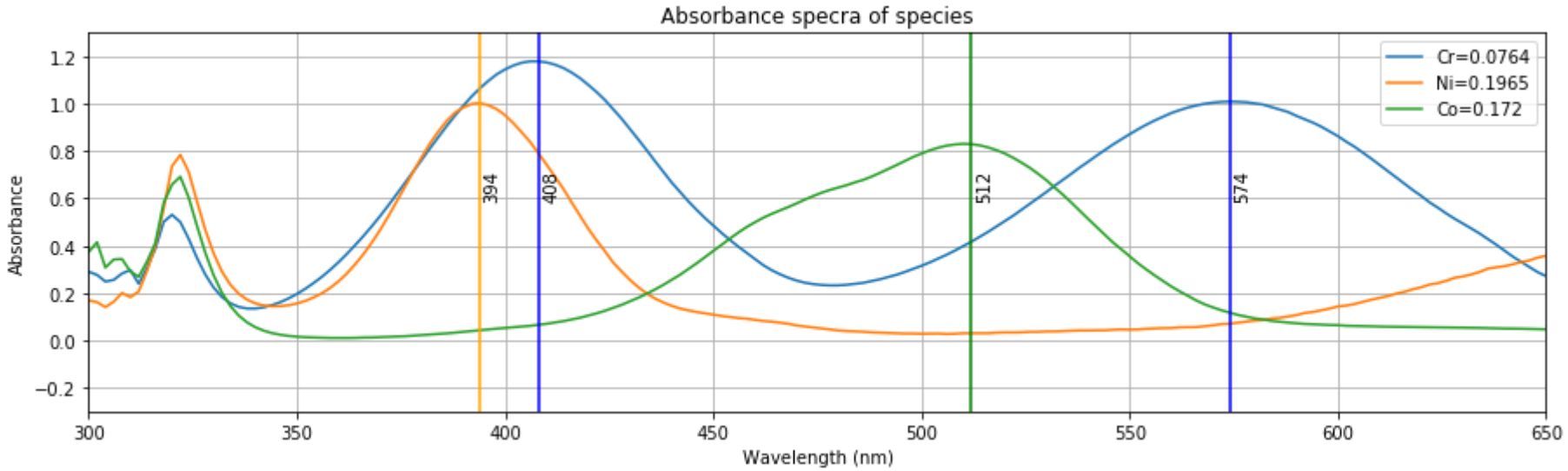
In [5]:
```
# Looping through each species to concatenate species name and its corresponding concentration in mol/litre
labels=[i+'='+str(j) for i,j in zip(species_con.columns,species_con.values.tolist()[0])]

plot_spectra(species_abs.T,labels,'Absorbance spectra of species',False)
```



Maximum absorption of energy are the unique features of each species

Species spectra with vertical lines marking the absorption peaks

In [6]:
```
plot_spectra(species_abs.T,labels,'Absorbance specra of species',True)
```



Maximum absorption of energy are seen at 408 nm and 574nm for Chromium, at 394 nm for Nickel and at 512nm for Cobalt of each species

Y - concentration of each species in the mixture

In [7]:
```
mixture_con.shape
```

Out[7]:
```
(130, 3)
```

In [8]:
```
mixture_con.head(6)
```

Out[8]:

	Cr	Ni	Co
0	0.003058	0.015715	0.006880
1	0.003058	0.015715	0.006880
2	0.003058	0.015715	0.006880
3	0.003058	0.015715	0.006880
4	0.003058	0.015715	0.006880
5	0.003058	0.015715	0.020639

X - absorption spectra of the mixture

In [9]:
```
mixture_abs.shape
```

Out[9]:
```
(130, 176)
```

In [10]:
```
mixture_abs.head(6)
```

Out[10]:

	300	302	304	306	308	310	312	314	316	318	...	632	634	636	638	
0	0.130158	0.308899	0.103867	0.118942	0.057755	-0.047806	0.158752	-0.000565	0.162003	0.046326	...	-0.045319	0.074310	0.000000	-0.075104	-0.1
1	0.317703	-0.013901	0.316162	0.258423	-0.011780	0.294006	-0.090881	-0.079285	0.139648	0.066483	...	-0.099518	0.086761	0.196930	0.366852	0.3
2	0.010635	0.030945	0.062988	0.256409	0.142258	0.429672	0.028778	0.244690	0.026642	-0.040924	...	0.180328	0.109253	0.045975	0.091019	-0.1
3	0.075134	-0.155594	0.177795	0.062973	0.015518	0.046707	0.305450	0.095108	-0.070251	0.302124	...	0.110184	-0.032288	0.264572	0.066071	0.1
4	0.241013	0.326935	-0.051743	0.162659	0.123138	0.227310	0.109894	-0.077850	0.165085	-0.007401	...	0.000000	0.110565	0.106537	0.073059	0.3
5	0.203171	-0.072968	0.167343	-0.052307	0.035309	-0.066238	-0.007797	0.293304	-0.077728	0.220978	...	0.077179	0.113647	-0.078979	0.155380	0.0

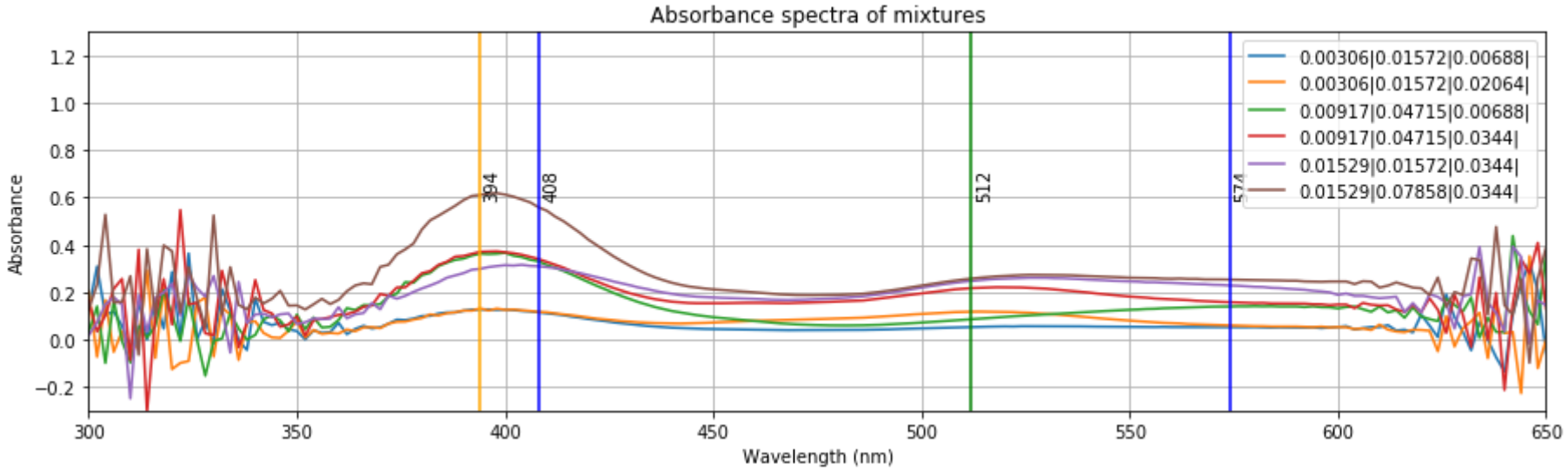
6 rows × 176 columns

Function to get the legend for the plot

In [11]:
```
'''
Function to get labels for the selected indices
Arguments: df (pandas.DataFrame), ind (list)
Returns: list of strings
'''
def get_labels(df,ind):
  mix_labels=[]
  for i in ind:
    label=''
    for j in range(3):
      label+=str(np.round(df.iloc[i,j],5))+'|'
    mix_labels.append(label)
  return mix_labels
```

Plot of absorbance spectra of selected mixtures from 130 samples

In [12]:
```
sel_ind=[0,5,60,70,100,129]
plot_spectra(mixture_abs.iloc[sel_ind,:].T,get_labels(mixture_con,sel_ind),'Absorbance spectra of mixtures',True)
```

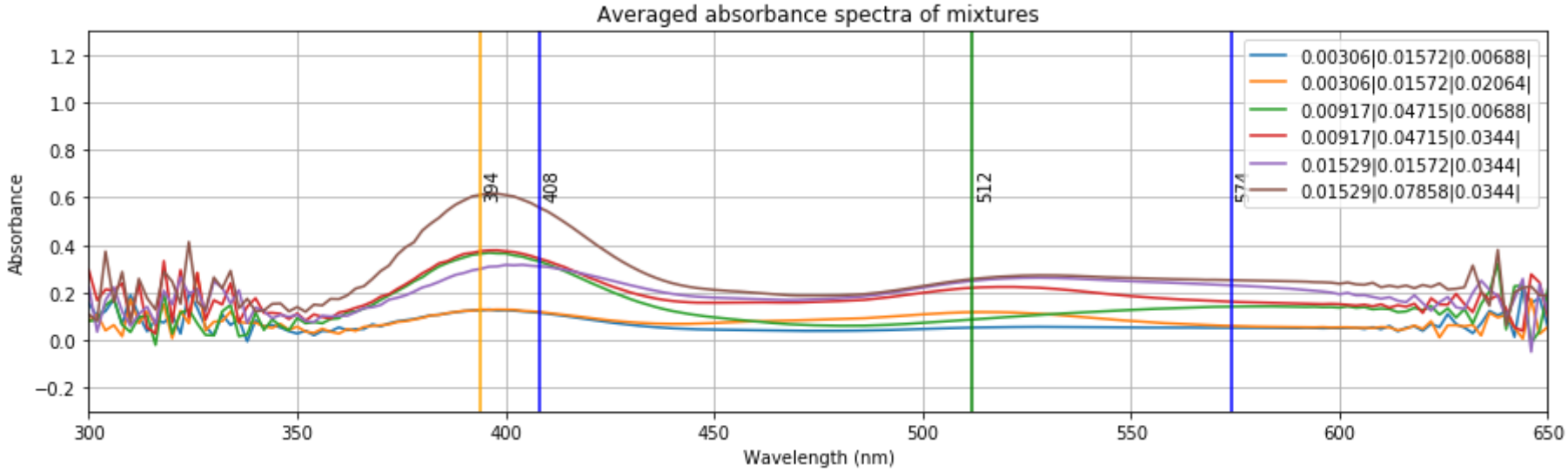


Averaging every 5 repeated experiments for each mixture of species concentration

In [13]:
```
mix_avg_abs=((mixture_abs + mixture_abs.shift(-1)+mixture_abs.shift(-2)+mixture_abs.shift(-3)+mixture_abs.shift(-4)) / 5)[::5]
mix_uniq_con=mixture_con[::5]
```

Plot of the averaged spectra of mixtures for every 5 samples

In [14]:
```
avg_sel_ind = [0,1,12,14,20,25]
plot_spectra(mix_avg_abs.iloc[avg_sel_ind,:].T,get_labels(mix_uniq_con,avg_sel_ind),
             'Averaged absorbance spectra of mixtures',True)
```



Questions

1. Can I predict concentration of each species in a given mixture using its absorption spectra?
2. How many species are there in the mixture?
3. What is the minimum number of principal components I should consider for a better prediction of the concentration of species in the mixture?

Principal Component Regression

In [15]:
```
# Importing model_selection library for using cross_validation
from sklearn import model_selection

# Importing the library for PCA
from sklearn.decomposition import PCA

# Importing the library for Linear Regression
from sklearn.linear_model import LinearRegression
```

Function performing linear regression over training and returns rmse of test predictions

In [16]:
```
'''
Function to linearly regress the training samples of X against Y
and to return the list of rmse for each variable in the output (y) of the testing samples

Arguments: X_train (numpy.ndarray),y_train (numpy.ndarray),X_test (numpy.ndarray),y_test (numpy.ndarray)
Returns: rmse (list of arrays)
'''

def linreg(X_train,X_test,y_train,y_test):
    ols = LinearRegression()
    ols.fit(X_train, y_train)
    y_pred = ols.predict(X_test)
    rmse=np.sqrt(((y_test-y_pred)**2).mean(axis=0)) #square root (mean square error)
    return rmse
```

Function iteratively performing linear regression between y and reduced sets of X in the increasing order of number of PCs over training and returns rmse of test predictions for each number of PCs considered.

In [17]:
```
'''
Function to perform linear regression using leave one out cross validation between Y
and reduced set of X iteratively from 1 principal component to maximum number of principal coomponents specified

Arguments: X (numpy.ndarray), y (numpy.ndarray), nfact (int)
Returns: RMSE_pcr_arr (numpy.ndarray of size nfact,number of variables of y)
'''

def pca_loocv_ols(X,y,nfact):
    RMSE_pcr_lst=list()
    for pc in range(1,nfact,1):   # Iterating over number of principal components
        pca = PCA(n_components=pc)  # Instantiating pca instance for each number of principal components in the iteration process
        X_red = pca.fit_transform(X)
        rmse_pcr_lst=list()
        lcv = model_selection.LeaveOneOut() # Instantiating an lcv instance
        for tr_idx, tst_idx in lcv.split(X_red): # interating through multiple folds
            X_train, X_test = X_red[tr_idx], X_red[tst_idx] # input X for both train and test
            y_train, y_test = y[tr_idx], y[tst_idx]   # output Y for both train and test
            rmse_pcr_lst.append(linreg(X_train,X_test,y_train,y_test)) # Appending rmse for each fold into a list
            #number of validations=26
        #number of PCR loops=25
        RMSE_pcr_lst.append(np.array(rmse_pcr_lst).mean(axis=0))
    return np.array(RMSE_pcr_lst)
```

Using one of the five measurements (first) for each mixture for modelling and estimating maximum error in the model

In [18]:
```
mix_sample_abs=mixture_abs[::5] # Sampling every first sample from the 5 experiments of same mixture proportions of species
std_y=np.array(mix_uniq_con).std(axis=0) # estimating standard deviation in the Y corresponding to maximum error in the model
std_y=std_y.reshape(1,-1) # reshaping the vector(Ny,) to array (1,Ny) where Ny is number of variables in output array
std_y
```

Out[18]:
```
array([[0.00493945, 0.0253862 , 0.01144835]])
```

Performing pcr over sampled spectra of mixtures

In [19]:
```
RMSE_pcr_samples=np.append(std_y,pca_loocv_ols(np.array(mix_sample_abs),np.array(mix_uniq_con),26),axis=0)
RMSE_pcr_samples.shape
```

Out[19]:
```
(26, 3)
```

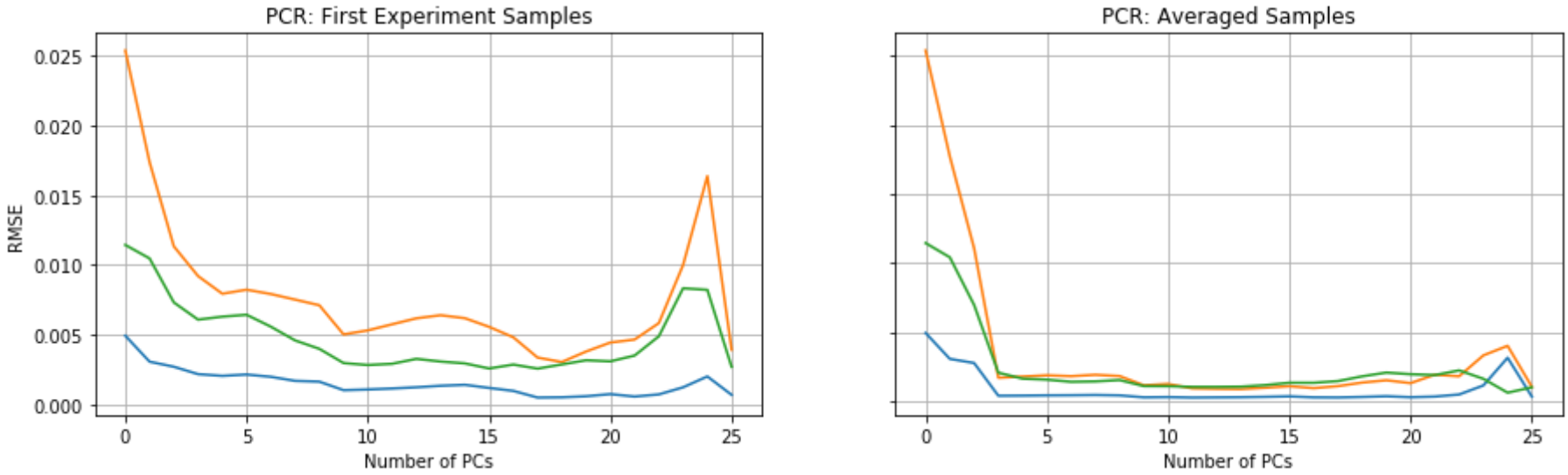
PCR over averaged X samples

In [20]:
```
RMSE_pcr_avg=np.append(std_y,pca_loocv_ols(np.array(mix_avg_abs),np.array(mix_uniq_con),26),axis=0)
RMSE_pcr_avg.shape
```

Out[20]:
```
(26, 3)
```

Plot of RMSE against number of PCs for both sampled and averaged spectra

In [21]:
```
fig, axs = subplots(1, 2,figsize=(15,4))
axs[0].plot(range(26),RMSE_pcr_samples)
axs[0].set_title('PCR: First Experiment Samples')
axs[1].plot(range(26),RMSE_pcr_avg)
axs[1].set_title('PCR: Averaged Samples')
axs[0].grid(True)
axs[1].grid(True)

for ax in axs.flat:
    ax.set(xlabel='Number of PCs', ylabel='RMSE')

for ax in axs.flat:
    ax.label_outer()
```



END OF SCRIPT

/